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specification

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Description

The present invention relates to a polyimide resin and film adhesive which has excellent heat resistance and low water absorption, which is suitable for use in electronics applications particularly as a material for mounting of semiconductor chips, which has excellent adhesion to silicon substrates and metals and which can be applied at low temperatures in a short period of time.

In recent years, while semiconductor chips have come to possess a higher function and a larger capacity and accordingly have become larger in size, the packages containing semiconductor chips are required to have an external form same as or even smaller than the conventional form so as to meet the demand for smaller electronic apparatuses. In response to this trend, some new mounting methods allowing the high-density mounting of high-density semiconductor chips have been proposed. One is a LOC (lead-on-chip) structure proposed for memory devices, wherein a die pad-free lead frame and chips are fixed to each other with a double-coated adhesive tape. Meanwhile, in logic devices, a multi-layered lead frame structure has been proposed in which the electric source and the glands are provided in different frames and the metal plates for heat radiation are provided in a plurality of layers. While in the conventional methods, the chip area was too large to secure the area for inner leads, in the above new methods, semiconductor chips and a lead frame are bonded with a double-coated adhesive tape and can be accommodated in a package having the same external form as the conventional package although the chip area is larger due to the larger capacity of chips. In the new methods, it is possible to rationalize in-chip wiring and wire bonding, shorten the length of wire for quicker signal, radiate the heat generated by the higher consumption of electric power, and make smaller the size of a device.

In the devices employing the above new mounting methods, there exist various adhesion interfaces between same materials or between different materials, such as chip vs. lead frame, lead frame vs. plate, lead frame vs. lead frame and the like. Therefore, the reliability of a device is greatly influenced by the adhesion reliabilities of said interfaces. The adhesion reliabilities must withstand the temperatures employed during the assembling of a device and further must be sufficient when the device is under humidity or under humidity and heat. Further, adhesion workability is also an important item. In semiconductor apparatuses of COL or LOC structure, the semiconductor chips and the lead frame are fixed to each other with an adhesive. This adhesive is required to have an excellent adhesivity so that the adhesion interfaces do not cause peeling under humidity or under thermal stresses caused by reflow soldering, temperature cycle, etc. The presence of a large amount of volatile components in the adhesive is not preferable because, when it is applied with heating, the volatile components contaminate the working environment, leads, etc. Desirably, the adhesive can complete adhesion in a period of time as short as possible, in view of the mass productivity of a device.

As such an adhesive, there have heretofore been used paste-like adhesives and adhesives obtained by coating an adhesive on a heat-resistant base. As the adhesive, there are used thermosetting resins of epoxy resin type, acrylic resin type or rubber-phenolic resin type; however, they do not satisfy the requirements for a highly reliable adhesive, because they contain a large amount of ionic impurities, require a high temperature and a long time for thermosetting and are not productive, generate a large amount of volatile matters during thermosetting and contaminate leads, and are highly hygroscopic. Thus, no satisfactory adhesive has not yet been found.

Meanwhile, with respect to the heat-resistant film adhesive which is contact-bondable with heating, some film adhesives are known. For example, hot-melt adhesives of polyamideimide type or polyamide type are described in Japanese Patent Application Kokai (Laid-Open) No. 282283/1989; a process for producing a flexible printed circuit board using a polyimide type adhesive is described in Japanese Patent Application Kokai (Laid-Open) No. 157190/1983; and thermosetting polyimide type film adhesives are described in Japanese Patent Application Kokai (Laid-Open) Nos. 235382/1987, 235383/1987 and 15663/1990. JP-A-61-241 359 (abstract) describes a polyimide precursor solution, obtained by reacting a specific diamino compound expressed by formula I [X is $C(CH_3)_2$, etc.] with a specific aromatic tetracarboxylic acid dianhydride (derivative) in a polyhydric alcohol expressed by formula II (m is ≥ 4), and containing 80~20mol% total of (A) a component consisting of repeating units expressed by formula III and/or formula IV (Ar_1 is 2,3,3',4'-biphenyltetracarboxylic acid residue; Ar_2 is 3,3',4,4'-benzophenonetetracarboxylic acid residue) and (B) a component consisting of repeating units expressed by formula V and/or formula VI (Ar_3 is 3,3',4,4'-biphenyltetracarboxylic acid residue; Ar_4 is pyromellitic acid residue) and (C) 20~80mol% component consisting of repeating units expressed by formula VII, etc. The ratio of the components (A) to (B) is 100~80mol% component (A) and 0~20mol% component (B). The polyimide precursor solution is stated to have good handleability without problems in safety and hygiene. However, the polyamide type or polyamideimide type resins have a drawback of high water absorption owing to the hydrophilicity of the amide group, and have had a limitation in using them as an adhesive for electronics applications wherein reliability is required. The thermosetting polyimide type film adhesives require the conditions for contact bonding with heating, of 275°C, 50 kg/cm² and 30 minutes, or must be cured from a semi-cured state at a high temperature for a long time, or generate condensation water during curing; therefore, they have been insufficient as an film adhesive for use in electronic parts which are sensitive to heat, pressure, water, etc. or in applications wherein mass productivity is required.

For the reasons mentioned above, it is desired to develop an adhesive suitable for the new mounting methods.

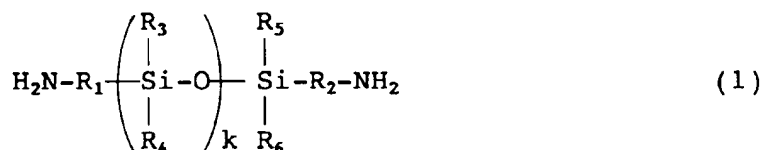
particularly an adhesive tape from productivity standpoint

Meanwhile, polyimide resins have high heat resistance, flame retardancy and excellent electrical insulating property and, accordingly, are in wide use in electric and electronic applications. However, conventional polyimide resins have high hygroscopicity and have no sufficient processability since they are insoluble and non-fusible or have very high melting points though they have excellent heat resistance. They are used as a material for mounting of semiconductors, in an insulating film between layers, a surface protective film, etc. In using them, a polyamic acid (a polyimide resin precursor) soluble in an organic solvent is coated on a semiconductor surface and the coated semiconductor is heated to remove the solvent and allow the imidization of the precursor to proceed. At that time, the acid amide type solvent used has a high boiling point and causes foaming of the resultant film, and a high-temperature (250°C or higher) drying step is necessary to evaporate the solvent completely and the device is inevitably exposed to a high temperature. These matters incur reduction in yield in the assembling step. Moreover, the conventional polyimide resins have high hygroscopicity and have caused, in some cases, a problem that the water absorbed by them is vaporized all at once at high temperatures to cause bulging or cracking.

The present inventors made extensive study in order to obtain a polyimide resin and film adhesive which can be applied at low temperatures in a short time, which has excellent heat resistance and which has low water absorption. As a result, the present inventors have found that a polyimide resin of particular structure achieves the above task, and have completed the present invention.

The present invention relates to a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, which polyimide resin is obtainable by reacting

- (A) 4,4'-oxydiphthalic acid dianhydride with a combination of the following amine components (C) and (D)
 (C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components: [2,2-bis-(4-(4-amino-phenoxy)phenyl)propane]



wherein R₁ and R₂ are each a bivalent aliphatic (C₁₋₄) or aromatic group; R₃, R₄, R₅ and R₆ are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

- (D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethylphenylene-diamine provided that 2,2-bis(4-(4-aminophenoxy)phenyl)propane is not the sole component (D)

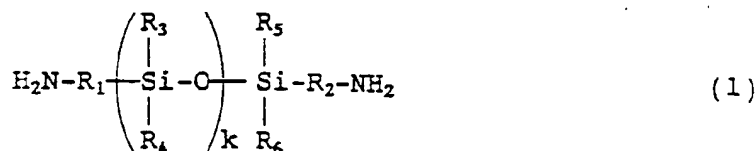
and converting the polyamic acid obtained into the polyimide resin.

Furthermore the invention relates to a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting

- (B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

- (C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R₁ and R₂ are each a bivalent aliphatic (C₁₋₄) or aromatic group; R₃, R₄, R₅ and R₆ are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

- (D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and a dimethyl-phenylene-diamine, and

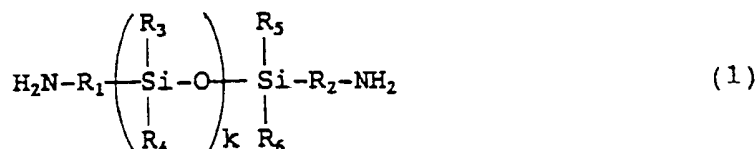
converting the polyamic acid obtained into the polyimide resin, and a polyimide resin having a glass transition temper-

ature of 350°C or lower and soluble in organic solvents, obtainable by reacting

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) a bis(aminophenoxy)benzene and 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a dimethyl-phenylene-diamine, and

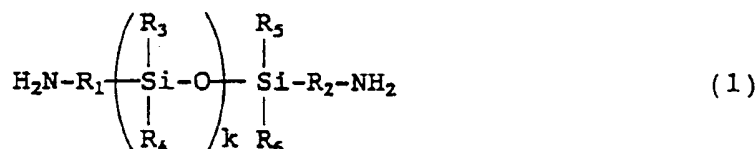
converting the polyamic acid obtained into the polyimide resin, and a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting a combination of the following acid components (A) and (B)

(A) 4,4'-oxydiphthalic acid dianhydride

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:

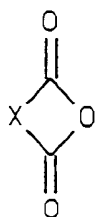


wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethyl-phenylene-diamine, and

converting the polyamic acid obtained into the polyimide resin.

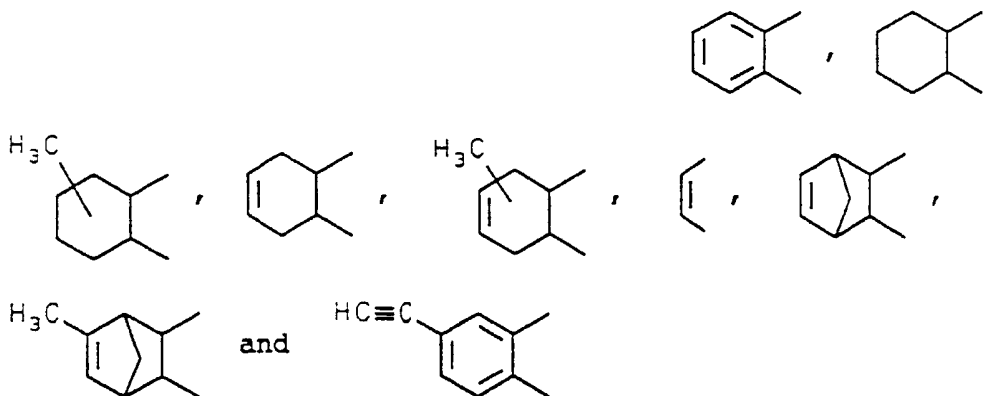
The present invention relates also to these resins, wherein the polyimide resin is capped, at the molecular ends, with an acid anhydride represented by the following general formula (2)



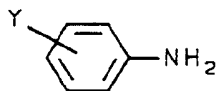
(2)

wherein

X is at least one group selected from



or an aromatic amine represented by the following general formula (3)



(3)

wherein Y is at least one group selected from hydrogen atom and methyl, ethyl, propyl, butyl, phenyl, methoxy, ethoxy, propoxy, butoxy and phenoxy groups.

Further embodiments are evident from the features of claims 6 to 14.

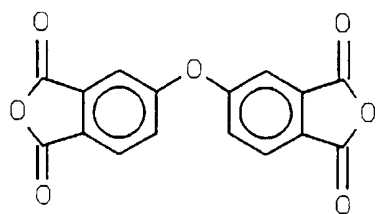
The present invention resides also to an adhesive film comprising a heat-resistant film base and any one of the polyimide resins applied on one side or both sides of the film base. Preferably the heat-resistant film base is a polyimide film having a glass transition temperature of 350°C or higher.

The present invention relates also to a process for producing an adhesive film, according to claims 17 to 25 which comprises casting, on one side or both sides of a substrate, an organic solvent solution of any one of the polyimide resins of the present invention.

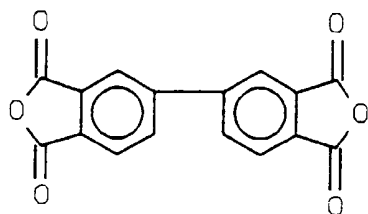
DETAILED DESCRIPTION OF THE INVENTION

4,4'-Oxydiphthalic acid dianhydride used in obtaining the polyimide resin of the present invention is represented by formula (4); 3,3',4,4'-biphenyltetracarboxylic acid dianhydride is represented by formula (5); 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride is represented by formula (6); 2,2-bis(4-(4-aminophenoxy)phenyl)propane is represented by formula (7); 1,3-bis(3-aminophenoxy)benzene, which is a typical example of a bis(aminophenoxy)benzene, is represented by formula (8); 2,5-dimethyl-p-phenylenediamine, which is a typical example of a dimethylphenylenediamine, is represented by formula (9); and α,ω -bis(3-aminopropyl)-polydimethylsiloxane, which is a typical example of the siloxane compound of the general formula (1), is represented by formula (10). In formula (10), k is preferably in the range of 4-10 in view of the glass transition temperature, adhesion and heat resistance of the polyimide resin. These siloxane compounds can be used not only singly but also in combination of two or more. Use of, in particular,

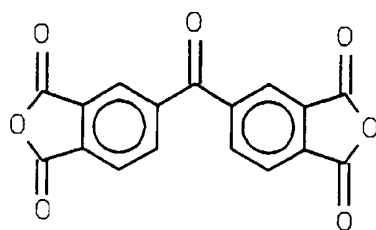
a blend of a siloxane compound of $k=1$ and a siloxane compound of $k=4-10$ is preferable for applications wherein adhesivity is very important.



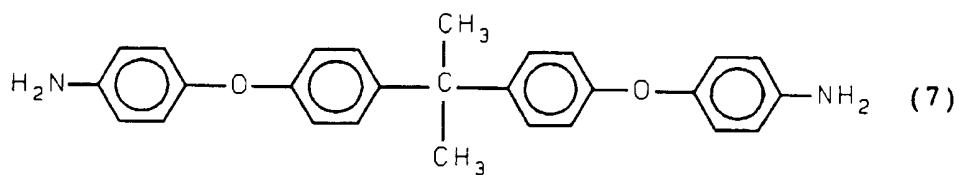
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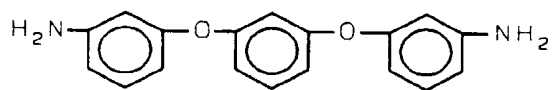
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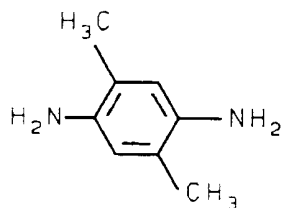
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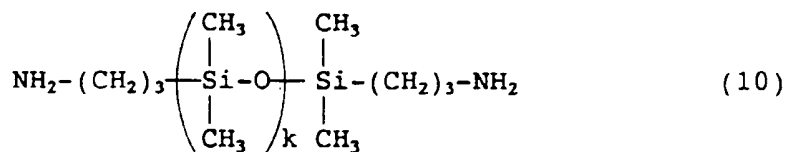
(7)



(8)



(9)



The bis(aminophenoxy)benzene is preferably 1,4-bis(3-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene or the like.

The dimethylphenylenediamine is preferably 2,5-dimethyl-p-phenylenediamine or 2,4-dimethyl-m-phenylenediamine.

It is important that the amount ratios of individual components be in the ranges as stated in the claims. The molar proportion of 4,4'-oxydiphthalic acid dianhydride, which is an important constituent of the acid components, or the siloxane compound is very important for the solubility of the polyimide resin obtained and, when said molar proportion is not in the above range, a feature of the present invention of being soluble in low-boiling solvents is lost. In formula (1), k is preferably 1-10, more preferably 4-10, and mixed use of a monomer of k=4-10 and a monomer of k=1 is particularly preferable. The amount of the α,ω -bisaminosiloxane compound represented by the general formula (1) is preferably 5-60% based on the total amine components. An amount of 5% or less is not preferred because the polyimide resin obtained has lower solubility in organic solvents, higher water absorption and lower wettability on an adhered to be applied, which makes adhesion in a short time difficult. An amount more than 60% is not preferred because the polyimide resin obtained has a very low glass transition temperature and has inferior properties at high temperatures, which incurs insufficient heat resistance.

The molar proportion of 2,2-bis(4-(4-aminophenoxy)phenyl)propane is preferably in the range of 10-90 mole% based on the total amine components. When the proportion is outside the range, problems arise in solubility and heat resistance.

Addition of dimethylphenylenediamine can increase the heat resistance of the polyimide resin obtained, without reducing its solubility in low-boiling solvents. Further, 1,3-bis(3-aminophenoxy)benzene can be added when the polyimide resin obtained is required to have low-temperature adhesion in adhesive applications.

In the present invention, the tetracarboxylic acid dianhydrides as the acid components further include, besides those mentioned above, for example, 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA), 2,2'-bis(4-(3,4-dicarboxyphenyl)phenyl)propane and 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride. One or more of these can be used together with the above-mentioned tetracarboxylic acid dianhydrides. Further, a dicarboxylic acid anhydride such as phthalic anhydride or the like can be added as a molecular weight modifier.

The tetracarboxylic acid dianhydride as an essential component is used in an amount of 50 mole% or more, preferably 70 mole% or more based on the total amount of acid components. An amount of less than 50 mole% is not preferred because the polyimide resin obtained has a too high glass transition temperature, which requires a very high temperature during adhesion, or has inferior adhesivity.

Similarly, the diamines include, besides the above-mentioned essential diamines, diamines such as 4,4'-diaminodiphenyl ether (4,4'-DDE), 3,3'-diaminodiphenyl ether (3,3'-DDE), 3,4'-diaminodiphenyl ether (3,4'-DDE), 4,4'-diaminodiphenyl sulfone (4,4'-DDS), 3,3'-diaminodiphenylsulfone (3,3'-DDS), 2,2-bis-4-aminophenylhexafluoropropane (BAPF), 2,2-bis-4-aminophenoxyphenylhexafluoropropane (BAPPF), bis-4-(4-aminophenoxy)phenylsulfone (BAPS), bis-4-(3-aminophenoxy)phenylsulfone (BAPSM), 4,4'-diaminobenzanilide (DABAN), m-phenylenediamine, p-phenylene-diamine, 4,4'-diaminodiphenylmethane (DDM), 2,4-diaminotoluene and the like. One or more of these can be used together with the essential diamines. The diamine compound as an essential component is used in an amount of 50 mole% or more, preferably 70 mole% or more based on the total diamine components. Similarly to the case of the acid components, an amount of 50 mole% or less is not preferred because various drawbacks are brought about, for example, the polyimide resin obtained has a high glass transition temperature, which requires a very high temperature during adhesion, or has inferior adhesivity.

The polyimide resin, by being capped at the molecular ends to control the molecular weight, can have a melt viscosity suitable for adhesion to a base and can have higher wettability for higher adhesivity. The amount of the end-capping agent, i.e. the acid anhydride or the aromatic amine is desirably in the range of 1-5 mole%. An amount less than 1 mole% is not preferred because the resulting polyimide resin has too large a molecular weight and is insoluble in low-boiling solvents in some cases, and has inferior wettability caused by the increase in melt viscosity, in applications where adhesivity is very important. When said amount is more than 5 mole%, the polyimide resin has a significantly reduced molecular weight and has a problem in heat resistance.

As the end-capping agent, there can be cited an acid anhydride represented by the general formula (2) and an aromatic amine represented by the general formula (3).

As the acid anhydride, there are used phthalic anhydride, maleic anhydride, nadic anhydride, etc. and, as the aromatic amine, there are used p-methylaniline, p-methoxyaniline, p-phenoxyaniline, etc.

In the polycondensation reaction, the molar ratio of the tetracarboxylic acid dianhydride components and the diamine components is an important factor which determines the molecular weight of the polyamic acid obtained. It is well known that there is a correlation between the molecular weight of a polymer and its properties, particularly between the number-average molecular weight and the mechanical properties. A larger number-average molecular weight gives superior mechanical properties. Accordingly, a polymer is required to have an appropriately high molecular weight in order for the polymer to show an excellent strength when put into practical use as an adhesive. In the present invention, the equivalent ratio r of the acid anhydride components to the amine components is in the range of preferably $0.950 \leq r \leq 1.06$, more preferably $0.975 \leq r \leq 1.06$, wherein $r = (\text{equivalent number of total acid components})/(\text{equivalent number of total amine components})$. When r is smaller than 0.950, the polyimide resin obtained has a small molecular weight, is fragile and therefore has low adhesivity. An r larger than 1.06 is not preferable because, in some cases, the unreacted carboxylic acids give rise to decarboxylation during heating and cause gas generation and foaming.

The reaction of the acid anhydrides and the amines is conducted in an aprotic polar solvent in a known way. The aprotic polar solvent is exemplified by N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), diglyme, cyclohexanone and 1,4-dioxane. The aprotic polar solvent may be used singly or as a mixture of two or more. At that time, a non-polar solvent compatible with the aprotic polar solvent may be used together with the aprotic polar solvent. An aromatic hydrocarbon such as toluene, xylene, solvent naphtha or the like is often used. The proportion of the non-polar solvent in the mixed solvent is preferably 30% by weight or less. The reason is that when the proportion of the non-polar solvent is 30% by weight or more, the mixed solvent has low solvency and may precipitate the polyamic acid formed. In the reaction of the tetracarboxylic acid dianhydrides with the diamines, sufficiently dried diamine components are dissolved in the above-mentioned reaction solvent which is dehydrated and purified; thereto are added sufficiently dried tetracarboxylic acid dianhydrides having a ring closure ratio of 98%, preferably 99% or higher to allow the reaction to proceed.

The thus-obtained polyamic acid solution is then heated in an organic solvent to give rise to dehydration, cyclization and resultantly imidization for formation of a polyimide. The water generated by the imidization reaction hinders the ring-closing reaction; therefore, an organic solvent non-compatible with water is added to the system and azeotropic distillation is conducted using an apparatus such as a Dean-Stark apparatus or the like, to discharge the water out of the system. Dichlorobenzene is known as the organic solvent non-compatible with water, but it may invite the presence of chlorine in the polyimide resin obtained. Hence, when the polyimide resin obtained is used in electronics applications, the above-mentioned aromatic hydrocarbon is used preferably. Further, it is possible to use, as a catalyst for imidization reaction, a compound such as acetic anhydride, β -picoline, pyridine or the like.

In the present invention, the degree of ring closure of imide is desired to be as high as possible. A low imidization degree is not preferable because, during adhesion, the heat generated gives rise to further imidization and consequently generates water. Desirably, an imidization degree of 95% or more, preferably 98% or more is achieved during the imidization.

In the imidization, if strong heating is conducted from the start before a polyimide film is formed, there is formed a rough surface or a partially stretched surface; therefore, it is preferable that heating be started at a low temperature and the temperature be increased slowly. For example, heating is conducted continuously from 100°C to 350°C in 0.5 hour or more. When the heating time is less than 0.5 hour, solvent removal becomes insufficient and ring closure of imide becomes insufficient and resultantly the polyimide resin obtained has no sufficient properties, although these matters vary depending upon the film thickness of the polyimide resin obtained. Alternatively, the temperature elevation may be conducted stepwise by conducting heating, for example, at 100°C for 30 minutes, then at 150°C for 30 minutes, at 200°C for 30 minutes, at 250°C for 30 minutes, at 300°C for 30 minutes and at 350°C for 30 minutes.

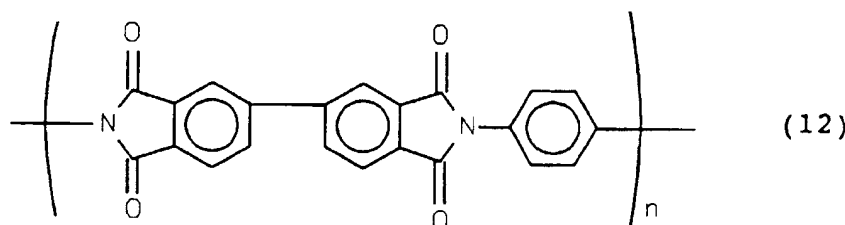
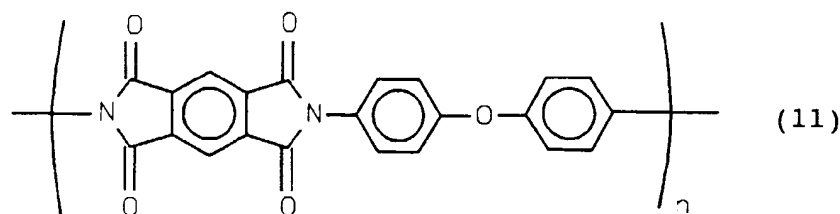
In the present invention, the thus-obtained polyimide solution is not coated on a substrate as it is, but is added to a poor solvent to reprecipitate the polyimide resin for removal of unreacted monomers and purification. The polyimide resin after purification, filtration and drying is redissolved in an organic solvent to prepare a coating composition. As the solvent, there is selected a solvent having a boiling point of 180°C or below in order to minimize the residual solvent in the film to be prepared and also in view of the economy and workability of the coating and drying steps of the varnish. In the present invention, there can be used, as ketone type solvents, acetone (b.p.: 56.5°C), methyl ethyl ketone (b.p.: 79.6°C), methyl isobutyl ketone (b.p.: 118°C), cyclopentanone (b.p.: 130.6°C) and cyclohexanone (b.p.: 155.6°C) and, as ether type solvents, 1,4-dioxane (b.p.: 101.1°C), tetrahydrofuran (b.p.: 66°C) and diglyme (b.p.: 162°C). These solvents may be used singly or in admixture of two or more. N,N-dimethylformamide and N,N-dimethylacetamide, both of which are amide type solvents, have boiling points of 180°C or below, respectively. They, however, are not preferred because they have high interaction with the polyimide resin and give a low evaporation rate and accordingly, unless drying is conducted at 200°C or above, it is difficult to remove the solvent molecules which are in solvation with the polyimide resin, and the solvent remains in the polyimide film in a large amount. Said solvents are not preferred, either, because they are highly hygroscopic and, when the polyimide coating composition containing them is made into a film

by coating, the film tends to absorb water and cause whitening. In the present invention, the residual solvent content in the film can be controlled at a low level, as compared with those in conventional polyimide films obtained by heating a polyamic acid dissolved in a high-boiling polar solvent (e.g. NMP) at the time of film formation to give rise to imidization, and further the contamination of an adhered by the thermal decomposition products of the polyimide resin can be prevented

To the polyimide resin coating composition can be added, if necessary various additives for imparting surface smoothness, such as smoothing agent, levelling agent, defoamer, adhesion improver and the like. An aromatic hydrocarbon type solvent can also be added in such an amount that it is uniformly soluble, in order to control the evaporation rate of the solvent in the polyimide resin coating composition.

In order to use the polyimide resin coating composition as an adhesive film, the polyimide resin coating composition is casted into a film shape and used as a film of polyimide resin alone or in one piece integrated with a film substrate.

In casting the polyimide resin coating composition, there can be used, for example, an apparatus in which a coating device (e.g. flow coater or roll coater) and a hot-air drying chamber are combined. The polyimide resin coating composition is coated on a substrate, and the coated substrate is introduced into a hot-air drying chamber and dried at a temperature and an air volume sufficient to evaporate the solvent in the coating composition. As the substrate, there can be used thin metal plates of stainless steel, aluminum, copper, etc. as well as plastic films such as polyimide film, biaxially stretched polyester film and the like. Of them, a polyimide resin film is most preferable because it has a small thermal expansion coefficient, excellent dimensional stability to temperature change, high flexibility, easy handleability, high adhesion to the adhesive resin of the present invention, etc. In particular, a film made of a polyimide resin having a structure represented by formula (11) or (12) is preferred.



When the polyimide resin is used as a film adhesive by itself, the polyimide resin film formed on a substrate is peeled off from the substrate and used. When the polyimide resin is used as one-piece adhesive integrated with a substrate, the polyimide resin film formed on one or both sides of a substrate is used as such.

The present invention can also be used as an adhesive of a two-layer or three-layer structure when the above substrate itself is used as a base. In that case, a polyimide film can be used advantageously as the substrate. However, in order for the adhesive of the present invention to sufficiently exhibit the characteristics of low water absorption and low ionic impurities content, the present adhesive preferably comprises only the polyimide resin of the present invention and contains neither a substrate nor a base. In the case where the polyimide resin is combined with a solvent having a boiling point of 180°C or below and a polyester film, no releasing agent (this agent is required when a metal substrate is used) is required and the polyimide resin can be easily peeled off from the polyester film. No use of a releasing agent (this agent hinders the adhesion property of the polyimide resin) is very advantageous in the production of an adhesive film, is most suited for the object of the present invention, and enables the best use of the heat resistance and high reliability of the polyimide.

How to use the polyimide adhesive of the present invention is not particularly restricted. It can be used as an adhesive film which can be contact-bonded with heating. That is, it is cut into a desired shape and contact-bonded with heating, using a heated heat block.

The adhesive film of the present invention is characterized by using, as a main constituent, a completely imidized

polyimide resin of particular structure soluble in low-boiling organic solvents. The polyimide resin as an adhesive can have a very low ionic-impurities level by being reprecipitated and purified, generates substantially no gas when heated because the imidization is conducted using a low-boiling solvent, has low water absorption and excellent heat resistance, and can be applied in a very short time as compared with thermosetting adhesives which give rise to a chemical reaction. The adhesive film of the present invention, by being processed into a tape shape, can have excellent adhesion workability and excellent dimensional precision to bonded portions.

The present invention is hereinafter described in more detail by way of Examples and Comparative Examples. However, the present invention is in no way restricted to these Examples.

Example 1

989 g of dehydrated and purified NMP was placed in a four-necked flask equipped with an inlet tube for dried nitrogen gas, a cooler, a thermometer and a stirrer, and was vigorously stirred for 10 minutes with nitrogen gas being passed therethrough. Then, thereto were added 58.47 g (0.200 mole) of 1,3-bis(3-aminophenoxy)benzene and 116.00 g (average molecular weight: 870, 0.133 mole) of α,ω -bis(3-aminopropyl)polydimethylsiloxane. The system was heated to 60°C and stirred until it became uniform. After the system became a uniform solution, it was cooled to 5°C in an ice water bath. Thereto were added, in 15 minutes, 81.07 g (0.261 mole) of 4,4'-oxydiphthalic acid dianhydride and 19.22 g (0.065 mole) of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride both of powder form. Thereafter, stirring was continued for 3 hours. During the stirring, the flask was kept at 5°C.

Then, the nitrogen gas inlet tube and the cooler were removed. A Dean-Stark tube filled with xylene was fitted to the flask and 109.9 g of xylene was added to the system. The system was heated to 200°C in an oil bath and the water generated was removed out of the system. In 4 hours of heating, the generation of water from the system was not seen. After cooling, the reaction mixture was placed in a large amount of methanol to precipitate a polyimide resin. The solid was collected by filtration and vacuum-dried at 80°C for 12 hours to remove the solvent. The resulting resin was measured for infrared absorption spectrum by a KBr tablet method, which gave an absorption at 5.6 μm by cyclic imide bond but no absorption at 6.06 μm by amide bond. Thus, it was confirmed that the resin was 100% imidized. 251.56 g (yield: 91.55%) of the thus-obtained polyimide resin was dissolved in cyclohexanone/toluene (90/10 w/w%) to prepare a polyimide resin varnish (resin content: 30%).

This polyimide resin varnish was coated on a polyimide film (UPILEX S manufactured by Ube Industries, Ltd.) having a thickness of 50 μm . The coated polyimide film was heat-dried in a circulating hot air dryer at 120°C for 0.5 hour and at 200°C for 1 hour. After cooling, the film was measured for thickness and the thickness of the formed adhesive layer was calculated. The adhesive layer had a thickness of 19 μm . The adhesion surface of the film showed no adhesiveness and was tack-free at room temperature.

This film adhesive was bonded to the metal luster surface of a 35- μm electrolytic copper foil, using a hot press having a heat block made of phosphor bronze, whereby a test piece was prepared. The adhesion conditions were such that contact bonding was conducted at 210°C for 2 seconds and, after pressure release, annealing was conducted at 210°C for 10 seconds. The pressure applied onto the adhesion surface was 4 kg/cm^2 as a result of calculation from the gauge pressure and the adhesion area. The test piece had a 180° peeling strength of 2.81 kgf/cm . Further, the 180° peeling strength after 168-hour treatment in an environment of 85°C and 85% was 2.66 kgf/cm . Thus, the adhesion surface of the film showed excellent adhesivity to copper. On the rupture surface, the adhesive resin layer caused cohesive failure and no foaming was seen. It indicated the excellent adhesivity of the adhesive resin layer to the base (polyimide film). There were also examined the adhesivities to a silicon wafer coated with a polyimide resin (SUMIRESIN EXCEL CRC-6061P manufactured by Sumitomo Bakelite Co., Ltd.). They were 2.01 kgf/cm and 1.75 kgf/cm , respectively. The results are shown in Table 1, together with other properties.

In the above, the molar ratios of the acids and the amines were $a/(a+b)=0.8$, $c/(c+d+e)=0.4$ and $(c+d)/(c+d+e)=1$, respectively.

Examples 2 to 5

Polyimide resin varnishes were prepared in the same manner as in Example 2 under the conditions shown in Table 1. They were coated on a polyimide film to prepare the respective film adhesives. Their properties are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Adhesive resin	Figures in parentheses indicate molar ratios				
Amine components	APB (60) APPS Si (40)	APB (65) APPS (35)	APB (75) APPS (25)	APB (60) APPS (25) BAPP (15)	APB (65) APPS (45)
Acid components	ODPA (80) BPDA (20)	ODPA (70) BTDA (30)	ODPA (100)	ODPA (100)	ODPA (90) PMDA (10)
Acid/amine molar ratio	0.980	0.985	0.995	0.995	0.985
Glass transition temperature	167°C	176°C	190°C	186°C	163°C
Thermal decomposition temperature	542°C	586°C	583°C	569°C	572°C
Linear expansion coefficient	6.3ppm	6.1ppm	3.4ppm	4.2ppm	8.3ppm
Adhesive layer thickness	19 µm	21 µm	20 µm	20 µm	19 µm
Heat-resistant base	UPILEX S 50 µm	UPILEX 50 µm	UPILEX S 50 µm	UPILEX S 50 µm	UPILEX S 50 µm
Adhesion conditions					
Temperature (°C)	210	210	210	210	240
Time (seconds)	20	25	10	10	10
Pressure (kg/cm ²)	4	4	4	4	6

- To be cont'd -

	Example 1	Example 2	Example 3	Example 4	Example 5
Peeling strength Ordinary state HHBT-168 Peeling interface	kgf/cm 2.81 2.66 Cohesive failure	2.39 2.11 Cohesive failure	1.96 1.72 Cohesive failure	2.09 1.85 Cohesive failure	2.63 2.23 Cohesive failure
Ionic impurities Cl ⁻ HCOO ⁻ (COO) ₂ ⁻ Na ⁺ NH ₄ ⁺	ppm 0.633 36.112 0.819 0.479 5.350	ppm 0.784 31.908 Not detected 0.627 2.989	ppm 0.488 32.437 0.977 0.163 4.883	ppm 0.531 30.798 0.774 0.382 3.192	ppm 0.779 35.674 0.859 0.531 4.992

Example 6

1,3-Bis(3-aminophenoxy)benzene, 2,2-bis(4-(4-aminophenoxy)phenyl)propane, α,ω -bis(3-aminopropyl)-polydimethylsiloxane (average molecular weight: 870), 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and 4,4'-oxydipthalic acid dianhydride were reacted in the same manner as in Example 1 at a molar ratio of 0.4/0.4/0.2/0.3/0.7, to obtain a polyimide resin. This polyimide resin was easily soluble in cyclohexanone and could be easily made into a polyimide resin film by using a polyester film as a substrate. The drying conditions were 120°C \times 0.5 hour and then 160°C \times 0.5 hour. The film had a glass transition temperature of 165°C, and was bonded to a copper foil at 240°C in 30 seconds and showed a peeling strength of 1.77 kgf/cm. The film after adhesion gave no foaming. Incidentally, the gas generated in the film was measured under the same conditions as in Table 2 and was 204 ppm.

Example 7

The polyimide resin solution obtained in Example 6 was coated on a polyimide film (UPILEX S manufactured by Ube Industries, Ltd.) having a thickness of 50 μ m, and a film adhesive was obtained in the same manner. This film had properties similar to those in Example 6.

Example 8

750 g of dehydrated and purified NMP was placed in a four-necked flask equipped with an inlet tube for dried nitrogen gas, a cooler, a thermometer and a stirrer, and was vigorously stirred for 10 minutes with nitrogen gas being passed therethrough. Then, thereto were added 73.0847 g (0.250 mole) of 1,3-bis(3-aminophenoxy)benzene (APB), 37.8163 g (average molecular weight: 840.36, 0.045 mole) of α,ω -bis(3-aminopropyl)polydimethylsiloxane (APPS) and 1.4971 g [0.006 mole, $k=1$ in formula (10)] of 1,3-bis(3-aminopropyl)tetramethyldisiloxane (APPS, $k=1$). The system was heated to 60°C and stirred until it became uniform. After the system became a uniform solution, it was cooled to 5°C in an ice water bath. Thereto was added, in 15 minutes, 93.4404 g (0.301 mole) of 4,4'-oxydipthalic acid dianhydride (ODPA) of powder form. Thereafter, stirring was continued for 3 hours. During the stirring, the flask was kept at 5°C.

Then, the nitrogen gas inlet tube and the cooler were removed. A Dean-Stark tube filled with xylene was fitted to the flask and 187 g of toluene was added to the system. The system was heated to 175°C in an oil bath and the water generated was removed out of the system. In 4 hours of heating, the generation of water from the system was not seen. After cooling, the reaction mixture was placed in a large amount of methanol to precipitate a polyimide resin. The solid was collected by filtration and vacuum-dried at 80°C for 12 hours to remove the solvent, whereby 186.28 g (yield: 90.5%) of a solid resin was obtained. The resin was measured for infrared absorption spectrum by a KBr tablet method, which gave an absorption at 5.6 μ m by cyclic imide bond but no absorption at 6.06 μ m by amide bond. Thus, it was confirmed that the resin was nearly 100% imidized. Incidentally, the molar ratios of the acids and the amines were $a/(a+b)=1$, $d/(c+d+e)=0.83$ and $e/(c+d+e)=0.17$, respectively.

The thus-obtained polyimide resin was dissolved in cyclohexanone/toluene (90/10 w/w%) to prepare a polyimide resin varnish having a solid content of 25%. This varnish was coated on one side of a polyimide film [UPILEX SGA (trade name) manufactured by Ube Industries, Ltd.] having a thickness of 50 μ m by use of a reverse roll coater to obtain a film adhesive in which the adhesive layer had a thickness of 30 μ m. The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. This film adhesive was hot-pressed onto a 35 μ m copper foil to prepare a test piece. The film adhesive was contact-bonded on the treated surface of the copper foil at 250°C for 2 seconds and, after pressure release, annealing was conducted at 250°C for 30 seconds. The pressure applied on the adhesion surface was 4 kgf/cm² as a result of calculation from the pressure gauge and the adhesion area. The test piece had a 180° peeling strength of 3.43 kgf/cm and showed excellent adhesivity. On the rupture surface, the adhesive resin caused cohesive failure and no foaming was seen. The results are shown in Table 2.

Example 9

The varnish of Example 8 was coated on a biaxially stretched polyester film [DIAFOIL (trade name) manufactured by Mitsubishi Rayon Co., Ltd.] having a thickness of 50 μ m. The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. After drying, the polyester film was removed by peeling to obtain a single-layer film of 32 μ m in thickness having no substrate. The peeling was easy and had no particular problem. The results when the film was bonded to the luster surface of a copper foil in the same manner as in Example 8, are shown in Table 2.

Examples 10-12

Reactions were conducted in the same manner as in Example 8, using the recipes shown in Table 2, to obtain soluble polyimide resins. Film adhesives were obtained using the polyimide resins. The results of evaluation for the film adhesives are shown in Table 2. Each of the film adhesives shows excellent properties.

10

15

20

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30

35

40

45

50

55

Table 2

Compo- sition	Items	Example	Example	Example	Example	Example	Example	Example	Example	Example
		8	9	10	11	12	1	2	1	2
Acid compo- nents	ODPA	100	100	80	100	80		PMDA 100		
	BTDA			20			30			
	BPDA					20	70			
Amine compo- nents	APB	83	83	60	15	45	30	65		
	BAPP				65	42				
	BAPPF			20						
	APPS (M=870)	15	15	20	20	10	4,4'-DDE 70			
Acid/amine equivalent ratio r	APPS (k=1)	2	2			3		35		
		1.00	1.00	1.00	1.00	0.99	0.98	0.99		

- To be cont'd -

Items	Example	Example	Example	Example	Example	Example	Comparative Example	Comparative Example
Varnish solvent	8	9	10	11	12		1	2
	Cyclo-hexa-none	Cyclo-hexa-none	Dioxane	Cyclo-hexa-none	Cyclo-hexa-none		Insol-uble	Insol-uble
Film drying conditions	180	180	170	180	180			
	Maximum temperature (°C)							
	6	6	6	6	6			
Constitution	UPILEX	Not used	UPILEX	Not used	Not used			
	Base							
	Thickness (μm)	50/30	20/50/20	25	25			
Properties	Condi-tions	Unit						
Water absorption	HH-168 treatment	z	0.59	0.19	0.56	0.23	0.30	
Generated gas	GC-MS method	ppm	95	81	78	101	96	
Generated water	Karl Fischer's method	z	0.32	0.16	0.29	0.23	0.20	

- To be cont'd -

Items		Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	E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In Table 2, ODPDA is an abbreviation of 4,4'-oxydiphthalic acid dianhydride; BTDA is an abbreviation of 4,4'-benzophenonetetracarboxylic acid dianhydride; BPDA is an abbreviation of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride; APB is an abbreviation of 1,3-bis(3-aminophenoxy)benzene; BAPPF is an abbreviation of 2,2-bis(4-(4-aminophenoxy)phenyl)hexafluoropropane; and APPS is an abbreviation of α,ω -bis(3-aminopropyl)polydimethylsiloxane.

The figures in composition column each indicate an equivalent ratio of each component in acid or amine components; water absorption refers to the saturated water absorption of total film when the film was allowed to stand in an environment of 85°C and 85% (relative humidity) for 168 hours (HH-168 treatment); generated gas refers to the amount measured by GC-MS method, of gas generated in total film when the film was heated at 250°C for 15 minutes; and generated water refers to the amount measured by Karl Fischer method, of water generated in total film when the film was heated at 250°C for 15 minutes.

Comparative Examples 1 and 2

Reactions were conducted in the same manner as in Example 8, using the recipes shown in Table 2, to obtain polyimide resins. Film adhesives were obtained using the polyimide resins. The results of evaluation for the film adhesives are shown in Table 2.

In Table 2, PMDA is an abbreviation of 1,2,4,5-benzenetetracarboxylic acid dianhydride; and 4,4'-DDE is an abbreviation of 4,4'-diaminodiphenyl ether.

As is clear from the above Examples, the present invention enables production of a film adhesive having high heat resistance and low hygroscopicity.

Example 13

755 g of dehydrated and purified NMP was placed in a four-necked flask equipped with an inlet tube for dried nitrogen gas, a cooler, a thermometer and a stirrer, and was vigorously stirred for 10 minutes with nitrogen gas being passed therethrough. Then, thereto were added 100.4400 g (0.120 mole) of α,ω -bis(3-aminopropyl)polydimethylsiloxane (APPS), 77.9978 g (0.190 mole) of 2,2-bis(4-(4-aminophenoxy)phenyl)propane (BAPP) and 10.8957 g (0.080 mole) of 2,5-dimethyl-p-phenylene-diamine (DPX). The system was heated to 60°C and stirred until it became uniform. After the system became a uniform solution, it was cooled to 5°C in an ice water bath. Thereto were added, in 15 minutes, 74.4533 g (0.240 mole) of 4,4'-oxydiphthalic acid dianhydride and 47.0752 g (0.160 mole) of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride both of powder form. Stirring was conducted for 1 hour, after which stirring was continued for 3 hours. During the stirring, the flask was kept at 5°C. Thereafter, 3.7046 g (0.020 mole) of p-phenoxyaniline (PPA) was added and stirring was continued for 1 hour.

Then, the nitrogen gas inlet tube and the cooler were removed. A Dean-Stark tube filled with xylene was fitted to the flask and 188 g of toluene was added to the system. The system was heated to 175°C in an oil bath and the water generated was removed out of the system. In 4 hours of heating, the generation of water from the system was not seen. After cooling, the reaction mixture was placed in a large amount of methanol to precipitate a polyimide resin. The solid was collected by filtration and vacuum-dried at 80°C for 12 hours to remove the solvent to obtain 284.99 g (yield: 90.6%) of a solid resin. The resin was measured for infrared absorption spectrum by a KBr tablet method, which gave an absorption at 5.6 μm by cyclic imide bond but no absorption at 6.06 μm by amide bond. Thus, it was confirmed that the resin was nearly 100% imidized.

The thus-obtained polyimide resin was dissolved in cyclohexanone/toluene (90/10 w/w%) to prepare a polyimide resin varnish having a solid content of 25%. This varnish was coated on one side of a polyimide film [UPILEX SGA (trade name) manufactured by Ube Industries, Ltd.] having a thickness of 50 μm , by use of a reverse roll coater to obtain an adhesive tape in which the adhesive layer had a thickness of 30 μm . The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. The adhesive tape was hot-pressed onto a 35 μm copper foil to prepare a test piece. The adhesive tape was contact-bonded on the treated surface of the copper foil at 250°C for 2 seconds and, after pressure release, annealing was conducted at 250°C for 30 seconds. The pressure applied onto the adhesion surface was 4 kgf/cm^2 as a result of calculation from the gauge pressure and the adhesion area. The test piece had a 180° peeling strength of 2.75 kgf/cm and showed excellent adhesivity. On the rupture surface, the adhesive resin layer caused cohesive failure and no foaming was seen. The results are shown in Table 3.

Example 14

The varnish of Example 13 was coated on a biaxially stretched polyester film [DIAFOIL (trade name) manufactured by Mitsubishi Rayon Co., Ltd.] having a thickness of 50 μm . The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. After drying, the polyester film was removed by peeling to obtain a single-layer film of 32 μm in thickness having no substrate. The peeling was easy and had no particular problem. The results when the

film was bonded to the luster surface of a copper foil in the same manner as in Example 13, are shown in Table 3.

Examples 15-18

5 Soluble polyimide resins were obtained in the same manner as in Example 13, under the conditions shown in Table 3. The results of evaluation for these polyimide resins are shown in Table 3. Each of the adhesive tapes shows excellent properties.

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Table 3

Compo- sition	Items	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Acid compo- nents	ODPA	60	60	80	80		80
	PMDA			17.5	17.5		
	BPDA	40	40			60	
	BTDA					40	19
	PA			5	5		2
Amine compo- nents	APPS	30	30	40	40	25	20
	BAPP	47.5	47.5	30	30	20	40
	APB					53	20
	DPX	20	20	30	30		20
Acid/amine equivalent ratio r	PPA	5	5			4	
		1.00	1.00	1.00	1.00	1.00	1.00
	Varnish solvent	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone

- To be cont'd -

Items	Example							
	13	14	15	16	17	18	18	18
Film drying conditions	Maximum temperature (°C)	180	180	180	180	180	180	180
	Time (min)	6	6	6	6	6	6	6
Tape constitution	Base	UPILEX	Not used	UPILEX	Not used	Not used	Not used	Not used
	Thickness (μm)	50/ 0	30	50/30	30	30	30	30
Tape properties	Condi- tions	Unit						
Water absorption	HH-168 treatment	0.65	0.31	0.58	0.26	0.26	0.34	0.34
Generated gas	GC-MS method	189	210	203	222	204	194	194
Generated water	Karl Fischer's method	0.58	0.28	0.61	0.32	0.27	0.31	0.31
Adhesion conditions	Tempera- ture	250	250	250	250	250	250	250
	Time	2/30	2/30	2/30	2/30	2/30	2/30	2/30
	Pressure	4/0	4/0	4/0	4/0	4/0	4/0	4/0

- To be cont'd -

Items	Example 13		Example 14		Example 15		Example 16		Example 17		Example 18	
	Adherend		Adherend		Adherend		Adherend		Adherend		Adherend	
Peeling strength	180° peeling	kgf/cm										

In Table 3, ODPa is an abbreviation of 4,4'-oxydiphthalic acid dianhydride; PMDA is an abbreviation of pyromellitic acid anhydride; PA is an abbreviation of phthalic anhydride; APPS is an abbreviation of α,ω -bis(3-aminopropyl)polydimethylsiloxane; BAPP is an abbreviation of 2,2-bis(4-(4-aminophenoxy)phenyl)propane; APB is an abbreviation of 1,3-bis(3-aminophenoxy)benzene; DPX is an abbreviation of 2,5-dimethyl-p-phenylenediamine; and PPA is an abbreviation of p-phenoxyaniline.

The figures in composition column each indicate an equivalent ratio of each component in acid or amine components; water absorption refers to the saturated water absorption of total film when the film was allowed to stand in an environment of 85°C and 85% (relative humidity) for 168 hours (HH-168 treatment).

Comparative Examples 3 and 4

Polyimide resins were obtained in the same manner as in Example 13 under the conditions shown in Table 4. The results of evolution for the polyimide resins are shown in Table 4.

Table 4

Items			Comparative Example 3	Comparative Example 4	
Composition	Acid components	ODPA			
		PMDA			
		BPDA	50	50	
		BTDA	47.5	47.5	
		PA	5	5	
	Amine components	APPS			
		BAPP	100	100	
		APB			
		DPX			
		PPA			
Acid/amine equivalent ratio r			1.00	1.00	
Varnish solvent			NMP	NMP	
Film drying conditions		Maximum temperature (°C)		250	200
		Time (min)		30	30
Tape constitution		Base		UPILEX	Not used
		Thickness (μm)		50/20	20
Tape properties		Conditions	Unit		
Water absorption		HH-168 treatment	%	1.15	0.87
Generated gas		GC-MS method	ppm	431	542
Generated water		Karl Fischer's method	%	0.78	0.58
Adhesion conditions		Temperature	°C	250	250
		Time	Seconds	2/30	2/30
		Pressure	kgf/cm ²	4/0	4/0
Adherend				Copper	Copper
Peeling strength		180° peeling	kgf/cm	0.78	(Foamed)

As clear from the above Examples and Comparative Examples, the present invention enables production of a

polyimide resin soluble in organic solvents and having high heat resistance and low hygroscopicity

Examples 19 and 20

Soluble polyimide resins were obtained in the same manner as in Example 13, under the conditions shown in Table 5. The results of evaluation for these polyimide resins are shown in Table 5. Each of the adhesive tapes shows excellent properties.

Table 5

Items		Example 19	Example 20	
Compo- sition	Acid compo- nents	ODPA	80	100
		BPDA		
		BTDA	19	
		PA	2	
	Amine compo- nents	BAPP	40	70
		APB	20	15
		DPX	20	
		APPS	20	15
		PPA		
	Acid/amine equivalent ratio r		1.00	1.00
Varnish solvent		Cyclo- hexanone	Cyclo- hexanone	
Film drying conditions		Maximum temperature (°C)	180	180
		Time (min)	6	6

- To be cont'd -

Items	Example 19		Example 20	
	UPILEX		Not used	
	50/30		30	
Base	Thickness (μm)		Unit	
	Condi- tions		z	
Tape constitution	HH-168 treatment		0.59	
Tape properties	GC-MS method		176	
Water absorption	Karl Fischer's method		0.47	
Generated gas	Temperature		250	
Generated water	Time		2/30	
Adhesion conditions	Pressure		4/0	
	Adherend		Copper	
Peeling strength	180° peeling		2.83	
			2.70	

In Table 5, ODPa is an abbreviation of 4,4'-oxydiphthalic acid dianhydride; BPDA is an abbreviation of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride; BTDA is an abbreviation of 4,4'-benzophenonetetracarboxylic acid dianhydride; PA is an abbreviation of phthalic anhydride; BAPP is an abbreviation of 2,2-bis(4-(4-aminophenoxy)phenyl)propane; APB is an abbreviation of 1,3-bis(3-aminophenoxy)benzene; DPX is an abbreviation of 2,5-dimethyl-p-phenylenediamine; APPS is an abbreviation of α,ω -bis(3-aminopropyl)polydimethylsiloxane; and PPA is an abbreviation of p-phenoxyaniline.

The figures in composition column each indicate an equivalent ratio of each component in acid or amine components; water absorption refers to the saturated water absorption when the film was allowed to stand in an environment of 85°C and 85% (relative humidity) for 168 hours (HH-168 treatment); generated gas refers to the amount measured by GC-MS method, of gas generated when the film was heated at 250°C for 15 minutes; and generated water refers to the amount measured by Karl Fischer method, of water generated when the film was heated at 250°C for 15 minutes. S in solubility column indicates "soluble in the relevant solvent".

Example 21

688 g of dehydrated and purified NMP was placed in a four-necked flask equipped with an inlet tube for dried nitrogen gas, a cooler, a thermometer and a stirrer, and was vigorously stirred for 10 minutes with nitrogen gas being

passed therethrough. Then, thereto were added 65.6823 g (0.160 mole) of 2,2-bis(4-(4-aminophenoxy)phenyl)propane (BAPP), 23.3869 g (0.08 mole) of 1,3-bis(3-aminophenoxy)benzene (APB), 10.8957 g (0.080 mole) of dimethylphenylenediamine (DPX) and 66.9600 g (average molecular weight: 837, 0.080 mole) of α,ω -bis(3-aminopropyl)polydimethylsiloxane (APPS). The system was heated to 60°C and stirred until it became uniform. After the system became a uniform solution, 2.3699 g (0.016 mole) of phthalic anhydride was added. The mixture was stirred for 1 hour. Then, the system was cooled to 5°C in an ice water bath. Thereto were added, in 15 minutes, 91.7966 g (0.312 mole) of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and 25.7784 g (0.08 mole) of 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride both of powder form. Then, stirring was continued for 3 hours.

Then, the nitrogen gas inlet tube and the cooler were removed. A Dean-Stark tube filled with xylene was fitted to the flask and 172 g of toluene was added to the system. The system was heated to 175°C in an oil bath and the water generated was removed out of the system. In 4 hours of heating, the generation of water from the system was not seen. After cooling, the reaction mixture was placed in a large amount of methanol to precipitate a polyimide resin. The solid was collected by filtration and vacuum-dried at 80°C for 12 hours to remove the solvent to obtain 257.32 g (yield: 89.7%) of a solid resin. The resin was measured for infrared absorption spectrum by a KBr tablet method, which gave an absorption at 5.6 μm by cyclic imide bond but no absorption at 6.06 μm by amide bond. Thus, it was confirmed that the resin was nearly 100% imidized. Incidentally, the molar ratios of the acid components and amine components were $a/(a+b+0.5f)=0.78$, $b/(a+b+0.5f)=0.2$ and $e/(c+d+e)=0.2$, respectively.

The thus-obtained polyimide resin was dissolved in cyclohexanone/toluene (90/10 w/w%) to prepare a polyimide resin varnish having a solid content of 25%. This varnish was coated on one side of a polyimide film [UPILEX SGA (trade name) manufactured by Ube Industries, Ltd.] having a thickness of 50 μm , by use of a reverse roll coater to obtain an adhesive tape in which the adhesive layer had a thickness of 30 μm . The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. The adhesive tape was hot-pressed onto a 35 μm copper foil to prepare a test piece. The adhesive tape was contact-bonded on the treated surface of the copper foil at 250°C for 2 seconds and, after pressure release, annealing was conducted at 250°C for 30 seconds. The pressure applied onto the adhesion surface was 4 kgf/cm^2 as a result of calculation from the gauge pressure and the adhesion area. The test piece had a 180° peeling strength of 3.12 kgf/cm and showed excellent adhesivity. On the rupture surface, the adhesive resin layer caused cohesive failure and no foaming was seen. The results are shown in Table 6.

Example 22

The varnish of Example 21 was coated on a biaxially stretched polyester film [DIAFOIL (trade name) manufactured by Mitsubishi Rayon Co., Ltd.] having a thickness of 50 μm . The drying temperature was 185°C (maximum temperature) and the drying time was 6 minutes. After drying, the polyester film was removed by peeling to obtain a single-layer film of 30 μm in thickness having no substrate. The peeling was easy and had no particular problem. The results when the film was bonded to the luster surface of a copper foil in the same manner as in Example 21, are shown in Table 6.

Examples 23-25

Soluble polyimide resins were obtained in the same manner as in Example 21, under the conditions shown in Table 6. The results of evaluation for these polyimide resins are shown in Table 6. Each of the adhesive tapes shows excellent properties.

Table 6

Items		Example 21	Example 22	Example 23	Example 24	Example 25	
Compo- sition	Acid compo- nents	BPDA	78	78	50	50	60
		BTDA	20	20	50	50	40
		PA	4	4			
	Amine compo- nents	BAPP	40	40	39	39	20
		APB	20	20			55
		DPX	20	20	30	30	
		APPS	20	20	30	30	25
		PPA			2	2	
Acid/amine equivalent ratio r		1.00	1.00	1.00	1.00	1.00	
Varnish solvent		Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	Cyclo- hexanone	
Film drying conditions	Maximum temperature (°C)	180	180	180	180	180	
	Time (min)	6	6	6	6	6	

- To be cont'd -

Items	Example 21		Example 22		Example 23		Example 24		Example 25	
	Base	Unit	Not used	UPILEX	UPILEX	Not used	Not used	Not used	Not used	Not used
Tape constitution	Thickness (μm)		30	50/30	50/30	30	30	30	30	30
Tape properties	Condi- tions	Unit								
Water absorption	HH-168 treatment	z	0.28	0.60	0.58	0.28	0.28	0.24		
Generated gas	GC-MS method	ppm	240	225	202	238	212			
Generated water	Karl Fischer's method	z	0.23	0.58	0.43	0.25	0.29			
Adhesion conditions	Tempera- ture	$^{\circ}\text{C}$	250	250	250	250	250	250		
	Time	Seconds	2/30	2/30	2/30	2/30	2/30	2/30		
	Pressure	kgf/cm^2	4/0	4/0	4/0	4/0	4/0	4/0		
Adherend			Copper	Copper	Copper	Copper	Copper	Copper		
Peeling strength	180 $^{\circ}$ peeling	kgf/cm	3.34	3.12	2.75	2.78	3.18			

In Table 6, BPDA is an abbreviation of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride; BTDA is an abbreviation of 4,4'-benzophenonetetracarboxylic acid dianhydride; PA is an abbreviation of phthalic anhydride; BAPP is an abbreviation of 2,2-bis(4-(4-aminophenoxy)phenyl)propane; APB is an abbreviation of 1,3-bis(3-aminophenoxy)benzene; DPX is an abbreviation of 2,5-dimethyl-p-phenylenediamine; APPS is an abbreviation of α,ω -bis(3-aminopropyl)polydimethylsiloxane; and PPA is an abbreviation of p-phenoxyaniline.

The figures in composition column each indicate an equivalent ratio of each component in acid or amine components: water absorption refers to the saturated water absorption of total film when the film was allowed to stand in an environment of 85°C and 85% (relative humidity) for 168 hours (HH-168 treatment); generated gas refers to the amount measured by GC-MS method, of gas generated from total film when the film was heated at 250°C for 15 minutes; and generated water refers to the amount measured by Karl Fischer method, of water generated from total film when the film was heated at 250°C for 15 minutes.

The present invention can provide an adhesive film of high reliability having both heat resistance and adhesion workability. The present adhesive film provides an advantage particularly when copper, which is easily oxidized, is used as a lead frame, because the present adhesive film can be applied at low temperatures in a short time without incurring the oxidation of copper surface. Further, since the present adhesive film is soluble in low-boiling solvents, the residual solvent content in the film can be controlled at a very low level by using mild drying conditions as compared with the drying conditions used for conventional polyimides. Furthermore, since the present adhesive film is already imidized, no high-temperature step is required for imidization and no water is generated, during the application of the adhesive. Thus, the present adhesive has features such as low water absorption, low impurities content, generation of very small amount of gas during heating, and the like; therefore, it has a very high industrial value as an electronics material in which high reliability and heat resistance are required, particularly as a material for mounting of semiconductors.

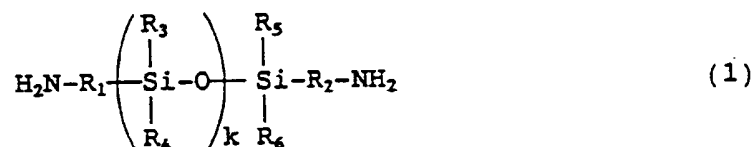
Claims

1. Polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting

(A) 4,4'-oxydiphthalic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20.

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethyl-phenylene-diamine provided that 2,2-bis(4-(4-aminophenoxy)phenyl)propane is not the sole component (D), and

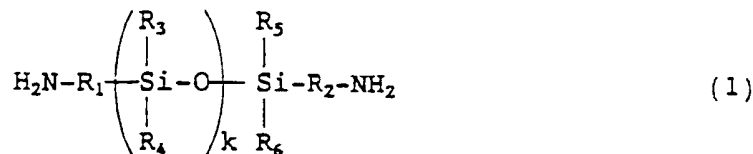
converting the polyamic acid obtained into the polyimide resin.

2. Polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and a dimethyl-phenylene-diamine, and

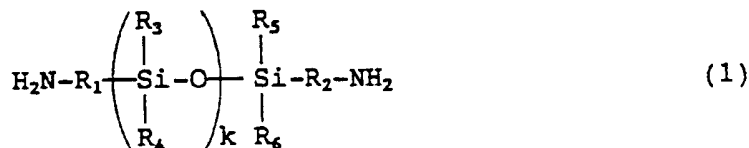
converting the polyamic acid obtained into the polyimide resin.

3. Polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) a bis(aminophenoxy)benzene and 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a dimethyl-phenylene-diamine, and

converting the polyamic acid obtained into the polyimide resin.

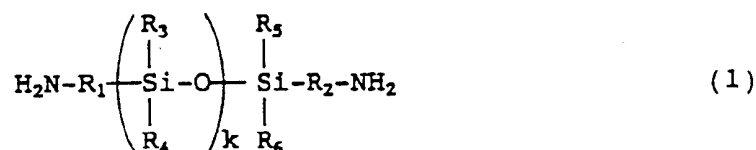
4. Polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, obtainable by reacting a combination of the following acid components (A) and (B)

(A) 4,4'-oxydipthalic acid dianhydride

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20.

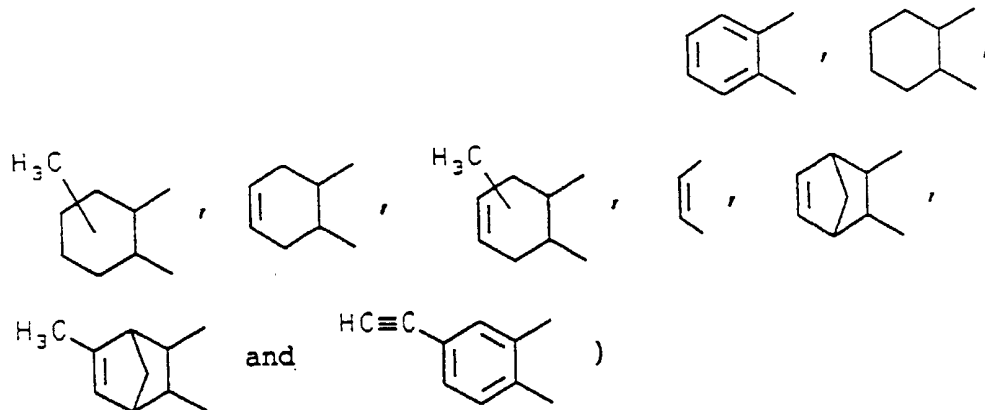
(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethyl-phenylene-diamine, and

converting the polyamic acid obtained into the polyimide resin.

5. Polyimide resin according to any one of claims 1 to 4, wherein the polyimide resin is capped, at the molecular ends, with an acid anhydride represented by the following general formula (2)



X is at least one group selected from



or an aromatic amine represented by the following general formula (3)



wherein Y is at least one group selected from hydrogen atom and methyl, ethyl, propyl, butyl phenyl methoxy, ethoxy, propoxy, butoxy and phenoxy groups.

6. Polyimide resin according to claim 1 or 4, wherein the polyimide resin is composed by using the acid component

(A), i.e., 4,4'-oxydiphthalic acid dianhydride in an amount of 60 mole% or more based on the total amount of the acid components.

7. Polyimide resin according to any one of claims 2 to 4, wherein the polyimide resin is composed by using, as the acid component (B), p moles of 3,3',4,4'-biphenyl-tetracarboxylic acid dianhydride and q moles of 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride in proportions satisfying $0.5 \leq p/(p+q) \leq 0.9$.
8. Polyimide resin according to any one of claims 1, 3 and 4, wherein the polyimide resin is composed by using, as the amine component (D), 1,3-bis(3-aminophenoxy)benzene in an amount of 10-90 mole% based on the total amount of the amine components.
9. Polyimide resin according to claim 4, wherein the polyimide resin is composed by using, as the acid components, a moles of 4,4'-oxydiphthalic acid dianhydride and b moles of another tetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylene-diamine and e moles of another diamine in proportions satisfying $a/(a+b) \geq 0.6$, $0.6 > b/(a+b) \geq 0$, $0.1 \leq c/(c+d+e) \leq 0.6$, $0.6 \leq (c+d)/(c+d+e)$, $0 \leq e/(c+d+e) < 0.6$ and $0.950 < (a+b)/(c+d+e) < 1.02$.
10. Polyimide resin according to claim 4, wherein the polyimide resin is composed of, as the acid components, a moles of 4,4'-oxydiphthalic acid dianhydride and b moles of another tetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylene-diamine and e moles of another diamine, and wherein the polyimide resin is capped, at the molecular ends, with f moles of an acid anhydride represented by general formula (2) or g moles of an aromatic amine represented by general formula (3), and wherein the molar ratios of a, b, c, d, e, f and g satisfy $0.6 \leq a/(a+b+0.5f)$, $0 \leq b/(a+b+0.5f) < 0.6$, $0.1 \leq c/(c+d+e+0.5g) \leq 0.6$, $0 \leq e/(c+d+e) < 0.6$, $0.01 \leq f/(a+b+0.5f) \leq 0.05$ and $0.01 \leq g/(c+d+e+0.5g) \leq 0.05$ and either of f and g is 0.
11. Polyimide resin according to claim 2 or 3, wherein the polyimide resin is composed by using as the acid components, p moles of 3,3',4,4'-biphenyltetra-carboxylic acid dianhydride and q moles of 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), c' moles of 2,2-bis(4-(4-aminophenoxy)phenyl)propane and d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylenediamine so that the molar ratios of p, q, c, c' and d satisfy $0.5 \leq p/(p+q) \leq 0.9$, $0.1 \leq c/(p+q) \leq 0.5$ and $0.05 \leq c/(c+c'+d) \leq 0.5$.
12. Polyimide resin according to claim 2 or 3, wherein the polyimide resin is composed of, as the acid components, p moles of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and q moles of 3,3',4,4'-benzophenone-tetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), c' moles of 2,2-bis(4-(4-aminophenoxy)phenyl)propane and d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylenediamine, and wherein the polyimide resin is capped, at the molecular ends, with f moles of an acid anhydride represented by general formula (2) or g moles of an aromatic amine represented by general formula (3), and wherein the molar ratios of p, q, c, c', d, f and g satisfy $0.5 \leq p/(p+q+0.5f) \leq 0.9$, $0.1 \leq q/(p+q+0.5f) \leq 0.5$, $0.05 \leq c/(c+c'+d+0.5g) \leq 0.5$, $0.01 \leq f/(p+q+0.5f) \leq 0.05$ and $0.01 \leq g/(c+c'+d+0.5g) \leq 0.05$ and either of f and g is 0.
13. Polyimide resin according to claim 4, wherein the polyimide resin is composed of, as the acid components, a moles of 4,4'-oxydiphthalic acid dianhydride and b moles of one or two tetracarboxylic acid dianhydrides selected from the group consisting of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), c' moles of 2,2-bis(4-(4-aminophenoxy)phenyl)propane and d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylenediamine so that the molar ratios of a, b, c, c' and d satisfy $a/(a+b) \geq 0.6$, $b/(a+b) \leq 0.4$ and $0.05 \leq c/(c+c'+d) \leq 0.5$.
14. Polyimide resin according to claim 4, wherein the polyimide resin is composed of, as the acid components, a moles of 4,4'-oxydiphthalic acid dianhydride and b moles of one or two tetracarboxylic acid dianhydrides selected from the group consisting of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride and, as the amine components, c moles of a siloxane compound represented by the general formula (1), c' moles of 2,2-bis(4-(4-aminophenoxy)phenyl)propane and d moles of 1,3-bis(3-aminophenoxy)benzene and/or dimethylphenylenediamine, and wherein the polyimide resin is capped, at the molecular ends, with f

moles of an acid anhydride represented by general formula (2) or g moles of an aromatic amine represented by general formula (3), and wherein the molar ratios of a, b, c, c', d, f and g satisfy $a/(a+b+0.5f) \geq 0.6$, $b/(a+b+0.5f) \leq 0.4$, $0.05 \leq c/(c+c'+d+0.5g) \leq 0.5$, $0.01 \leq f/(a+b+0.5f) \leq 0.05$ and $0.01 \leq g/(c+c'+d+0.5g)$ and either of f and g is 0.

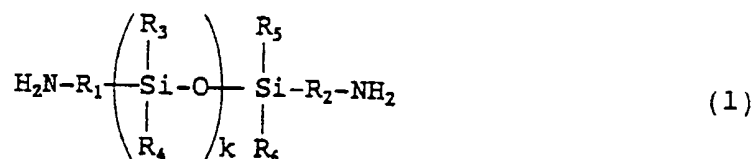
15. Adhesive film comprising a heat-resistant film base and a polyimide resin of any of claims 1 to 14 applied on one side or both sides of the film base.

16. Adhesive film according to claim 15, wherein the heat-resistant film base is a polyimide film having a glass transition temperature of 350°C or higher.

17. A process for producing an adhesive film, which comprises casting, on one side or both sides of a substrate, an organic solvent solution of a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, said polyimide resin being obtained by reacting

(A) 4,4'-oxydiphthalic acid dianhydride with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethylphenylene-diamine, and

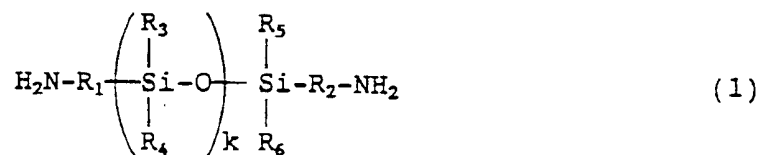
converting the polyamic acid obtained into the polyimide resin.

18. A process for producing an adhesive film, which comprises casting on one side or both sides of a substrate, an organic solvent solution of a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, said polyimide resin being obtained by reacting

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20,

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and a dimethylphenylene-diamine, and

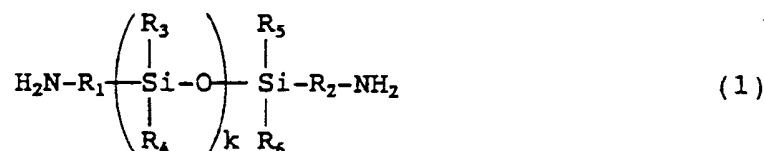
converting the polyamic acid obtained into the polyimide resin.

19. A process for producing an adhesive film, which comprises casting, on one side or both sides of a substrate, an organic solvent solution of a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, said polyimide resin being obtained by reacting

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:



wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group, and k is an integer of 1-20.

(D) a bis(aminophenoxy)benzene and 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a dimethylphenylene-diamine, and

converting the polyamic acid obtained into the polyimide resin.

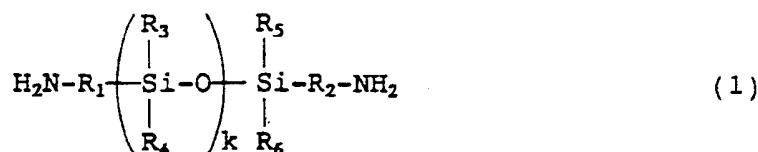
20. A process for producing an adhesive film, which comprises casting, on one side or both sides of a substrate, an organic solvent solution of a polyimide resin having a glass transition temperature of 350°C or lower and soluble in organic solvents, said polyimide resin being obtained by reacting a combination of the following acid components (A) and (B)

(A) 4,4'-oxydiphthalic acid dianhydride

(B) 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and/or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

with a combination of the following amine components (C) and (D)

(C) 60 to 5% by mole of a siloxane compound represented by the following general formula (1), based on the total amount of the amine components:

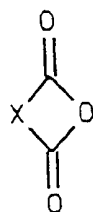


wherein R_1 and R_2 are each a bivalent aliphatic (C_{1-4}) or aromatic group; R_3 , R_4 , R_5 and R_6 are each a monovalent aliphatic or aromatic group; and k is an integer of 1-20.

(D) 2,2-bis(4-(4-aminophenoxy)phenyl)propane and/or a bis(aminophenoxy)benzene and/or a dimethylphenylene-diamine, and

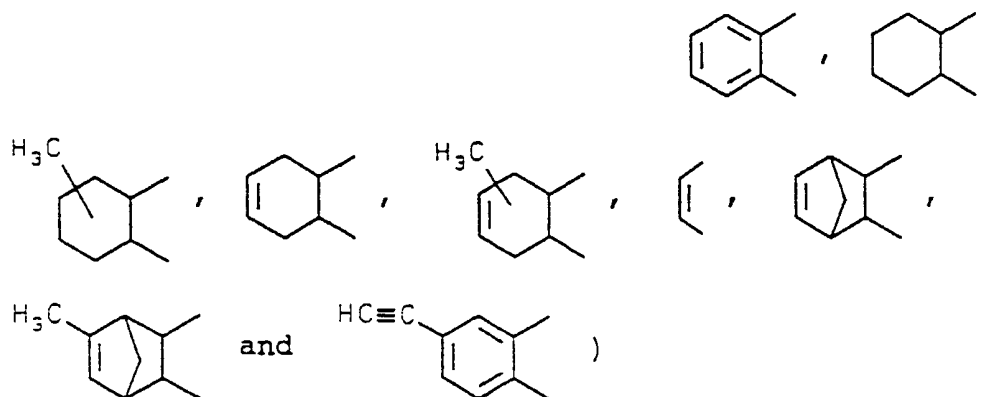
converting the polyamic acid obtained into the polyimide resin.

21. A process for producing an adhesive film according to any one of claims 17 to 20, wherein the polyimide resin is capped, at the molecular ends, with an acid anhydride represented by the following general formula (2)

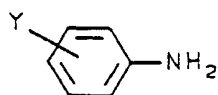


(2)

X is at least one group selected from



or an aromatic amine represented by the following general formula (3)



(3)

wherein Y is at least one group selected from hydrogen atom and methyl, ethyl, propyl, butyl, phenyl, methoxy, ethoxy, propoxy, butoxy and phenoxy groups.

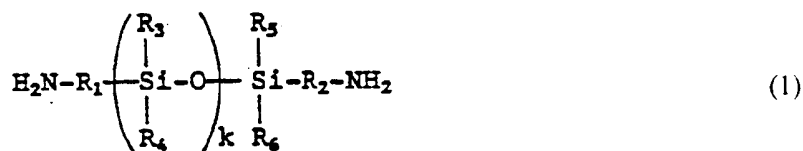
22. A process for producing an adhesive film according to any one of claims 17 to 21, wherein the substrate is a polyimide film having a glass transition temperature of 350°C or higher.
23. A process for producing an adhesive film according to any one of claims 17 to 21, which comprises peeling the substrate after casting and drying.
24. A process according to claim 23, wherein the substrate is a biaxially stretched polyester film.
25. A process for producing an adhesive film according to any one of claims 17 to 24, which comprises casting said polyimide resin solution on a substrate by use of an organic solvent having a boiling point of 180°C or lower, drying the cast polyimide resin solution and peeling the dried polyimide resin from the substrate.

Patentansprüche

1. Polyimidharz mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, erhältlich durch Umsetzung von
(A) 4,4'-Oxydiphthalsäureanhydrid
mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die

Gesamtmenge der Amin-Komponenten,



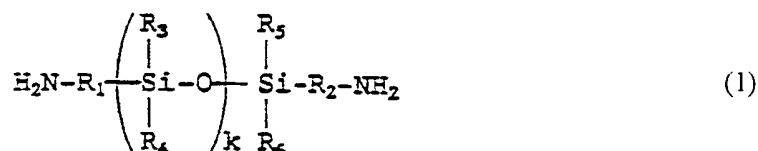
wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind und k eine ganze Zahl von 1-20 ist,

(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Bis-(aminophenoxy)-benzol und/oder ein Dimethyl-phenylen-diamin, mit der Maßgabe, daß 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan nicht die alleinige Komponente (D) ist, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz

2. Polyimidharz mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, erhältlich durch Umsetzung von
(B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



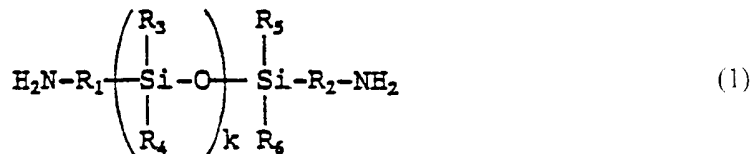
wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind und k eine ganze Zahl von 1-20 ist,

(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und ein Dimethyl-phenylen-diamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

3. Polyimidharz mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, erhältlich durch Umsetzung von
(B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste

R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind und k eine ganze Zahl von 1-20 ist,

(D) ein Bis-(aminophenoxy)-benzol und 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Dimethyl-phenylen-diamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

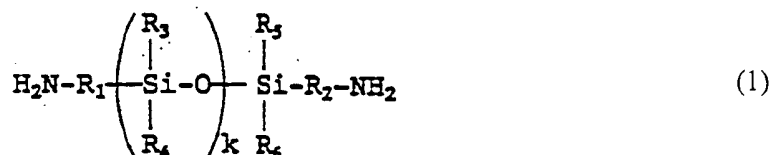
4. Polyimidharz mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, erhältlich durch Umsetzung einer Kombination der nachstehenden Säure-Komponenten (A) und (B)

(A) 4,4'-Oxydiphthalsäuredianhydrid,

(B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid

mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind und k eine ganze Zahl von 1-20 ist,

(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Bis-(aminophenoxy)-benzol und/oder ein Dimethyl-phenylen-diamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

5. Polyimidharz nach einem der Ansprüche 1 bis 4, wobei das Polyimidharz an seinen Molekülenden abgeschlossen ist mit einem Säureanhydrid der nachstehenden allgemeinen Formel (2)

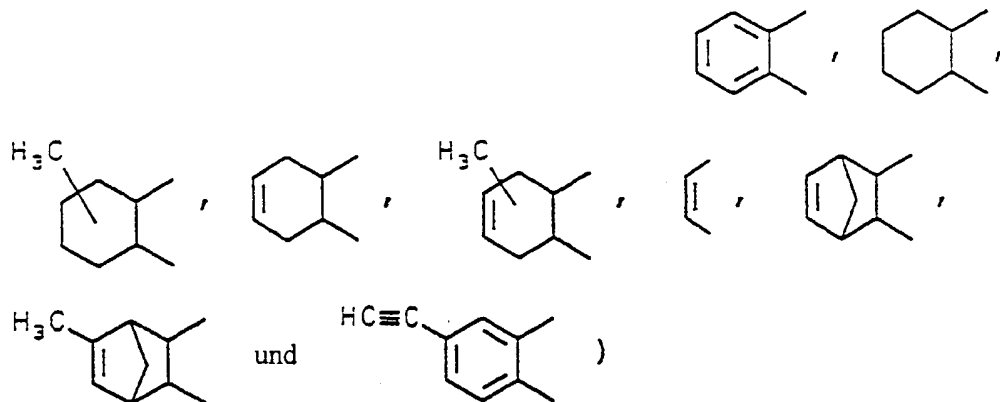


wobei X mindestens ein Rest ist, ausgewählt aus

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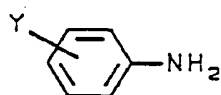
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oder einem aromatischen Amin der nachstehenden allgemeinen Formel (3)

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(3)

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wobei der Rest Y mindestens ein Rest ist, ausgewählt aus Wasserstoffatomen und Methyl-, Ethyl-, Propyl-, Butyl-, Phenyl-, Methoxy-, Ethoxy-, Propoxy-, Butoxy- und Phenoxyresten.

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6. Polyimidharz gemäß Anspruch 1 oder 4, wobei das Polyimidharz gebildet wird unter Verwendung der Säure-Komponente (A), d.h. 4,4'-Oxydiphthalsäuredianhydrid in einer Menge von 60 Mol-% oder mehr, bezogen auf die Gesamtmenge der Säure-Komponenten.

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7. Polyimidharz gemäß einem der Ansprüche 2 bis 4, wobei das Polyimidharz gebildet wird unter Verwendung, als Säure-Komponente (B), von p Mol 3,3',4,4'-Biphenyl-tetracarbonsäuredianhydrid und q Mol 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid in Anteilen, die die Gleichung $0,5 \leq p/(p+q) \leq 0,9$ erfüllen.

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8. Polyimidharz gemäß einem der Ansprüche 1, 3 und 4, wobei das Polyimidharz gebildet wird unter Verwendung, als Amin-Komponente (D), von 1,3-Bis-(3-aminophenoxy)-benzol in einer Menge von 10-90 Mol-% bezogen auf die Gesamtmenge der Amin-Komponenten.

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9. Polyimidharz gemäß Anspruch 4, wobei das Polyimidharz gebildet wird unter Verwendung, als Säure-Komponenten, von a Mol 4,4'-Oxydiphthalsäuredianhydrid und b Mol eines weiteren Tetracarbonsäuredianhydrids und, als Amin-Komponenten, von c Mol einer Siloxanverbindung der allgemeinen Formel (1), d Mol 1,3-Bis-(3-aminophenoxy)-benzol und/oder Dimethylphenylen-diamin und e Mol eines weiteren Diamins in Anteilen, die die folgenden Bedingungen erfüllen, $a/(a+b) \geq 0,6$, $0,6 > b/(a+b) \geq 0$, $0,1 \leq c/(c+d+e) \leq 0,6$, $0,6 \leq (c+d)/(c+d+e)$, $0 \leq e/(c+d+e) < 0,6$ und $0,950 < (a+b)/(c+d+e) < 1,02$.

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10. Polyimidharz gemäß Anspruch 4, wobei das Polyimidharz zusammengesetzt ist aus, als den Säure-Komponenten, a Mol 4,4'-Oxydiphthalsäuredianhydrid und b Mol eines weiteren Tetracarbonsäuredianhydrids und, als den Amin-Komponenten, c Mol einer Siloxanverbindung der allgemeinen Formel (1), d Mol 1,3-Bis-(3-aminophenoxy)-benzol und/oder Dimethylphenylen-diamin und e Mol eines weiteren Diamins, und wobei das Polyimidharz an seinen Molekülenden abgeschlossen ist mit f Mol eines Säureanhydrids der allgemeinen Formel (2) oder g Mol eines aromatischen Amins der allgemeinen Formel (3), und wobei die Molverhältnisse von a, b, c, d, e, f und g die nachstehenden Bedingungen erfüllen, $0,6 \leq a/(a+b+0,5f)$, $0 \leq b/(a+b+0,5f) < 0,6$, $0,1 \leq c/(c+d+e+0,5g) \leq 0,6$, $0 \leq e/(c+d+e) < 0,6$, $0,01 \leq f/(a+b+0,5f) \leq 0,05$ und $0,01 \leq g/(c+d+e+0,5g) \leq 0,05$ und entweder f oder g ist 0.

11. Polyimidharz nach Anspruch 2 oder 3, wobei das Polyimidharz gebildet wird unter Verwendung, als den Säure-Komponenten, von p Mol 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und q Mol 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid und, als den Amin-Komponenten, von c Mol einer Siloxanverbindung der allgemeinen Formel

(1), c' Mol 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und d Mol 1,3-Bis-(3-aminophenoxy)-benzol und/oder Dimethylphenylendiamin, so daß die Molverhältnisse von p, q, c, c' und d die nachstehenden Bedingungen erfüllen, $0,5 \leq p/(p+q) \leq 0,9$, $0,1 \leq q/(p+q) \leq 0,5$ und $0,05 \leq c/(c+c'+d) \leq 0,5$.

12. Polyimidharz nach Anspruch 2 oder 3, wobei das Polyimidharz zusammengesetzt ist aus, als den Säurekomponenten, p Mol 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und q Mol 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid und, als den Amin-Komponenten, c Mol einer Siloxanverbindung der allgemeinen Formel (1), c' Mol 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und d Mol 1,3-Bis-(3-aminophenoxy)-benzol und/oder Dimethylphenylendiamin, und wobei das Polyimidharz an seinen Molekülenden abgeschlossen ist mit f Mol eines Säureanhydrids der allgemeinen Formel (2) oder g Mol eines aromatischen Amins der allgemeinen Formel (3), und wobei die Molverhältnisse von p, q, c, c', d, fund g die nachstehenden Bedingungen erfüllen, $0,5 \leq p/(p+q+0,5f) \leq 0,9$, $0,1 \leq q/(p+q+0,5f) \leq 0,5$, $0,05 \leq c/(c+c'+d+0,5g) \leq 0,5$, $0,01 \leq f/(p+q+0,50) \leq 0,05$ und $0,01 \leq g/(c+c'+d+0,5g) \leq 0,05$ und entweder f oder g ist 0.

13. Polyimidharz gemäß Anspruch 4, wobei das Polyimidharz zusammengesetzt ist aus, als den Säure-Komponenten, a Mol 4,4'-Oxydiphthalsäuredianhydrid und b Mol von einem oder zwei Tetracarbonsäuredianhydriden, ausgewählt aus der Gruppe, bestehend aus 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid und, als den Amin-Komponenten, c Mol einer Siloxanverbindung der allgemeinen Formel (1), c' Mol 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und d Mol 1,3-Bis-(3-aminophenoxy)benzol und/oder Dimethylphenylendiamin, so daß die Molverhältnisse von a, b, c, c' und d die folgenden Bedingungen erfüllen, $a/(a+b) \geq 0,6$, $b/(a+b) \leq 0,4$ und $0,05 \leq c/(c+c'+d) \leq 0,5$.

14. Polyimidharz gemäß Anspruch 4, wobei das Polyimidharz zusammengesetzt ist aus, als den Säure-Komponenten, a Mol 4,4'-Oxydiphthalsäuredianhydrid und b Mol von einem oder zwei Tetracarbonsäuredianhydriden, ausgewählt aus der Gruppe, bestehend aus 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid und, als den Amin-Komponenten, c Mol einer Siloxanverbindung der allgemeinen Formel (1), c' Mol 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und d Mol 1,3-Bis-(3-aminophenoxy)benzol und/oder Dimethylphenylendiamin, und wobei das Polyimidharz an seinen Molekülenden abgeschlossen ist mit f Mol eines Säureanhydrids der allgemeinen Formel (2) oder g Mol eines aromatischen Amins der allgemeinen Formel (3), und wobei die Molverhältnisse von a, b, c, c', d, fund g die folgenden Bedingungen erfüllen, $a/(a+b+0,5f) \geq 0,6$, $b/(a+b+0,5f) \leq 0,4$, $0,05 \leq c/(c+c'+d+0,5g) \leq 0,5$, $0,01 \leq f/(a+b+0,5f) \leq 0,05$ und $0,01 \leq g/(c+c'+d+0,5g)$ und entweder f oder g ist 0.

15. Klebstoffilm, umfassend eine wärmebeständige Filmgrundlage und ein Polyimidharz nach einem der Ansprüche 1 bis 14, das auf einer Seite oder beiden Seiten der Filmgrundlage aufgetragen ist.

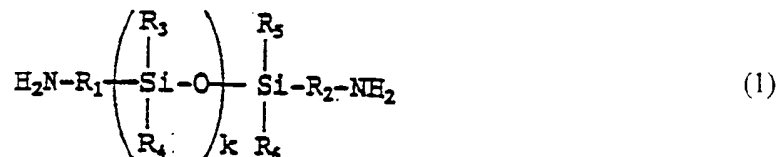
16. Klebstoffilm gemäß Anspruch 15, wobei die wärmebeständige Filmgrundlage ein Polyimidfilm mit einer Glasübergangstemperatur von 350°C oder höher ist.

17. Ein Verfahren zur Herstellung eines Klebstoffilms, umfassend das Aufbringen, auf einer Seite oder beiden Seiten eines Substrats, einer Lösung in einem organischen Lösungsmittel eines Polyimidharzes mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, wobei das Polyimidharz erhalten wird durch Umsetzung von

(A) 4,4'-Oxydiphthalsäuredianhydrid,

mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



wobei die Reste R₁ und R₂ jeweils ein zweiwertiger aliphatischer (C₁₋₄) oder aromatischer Rest sind, die Reste

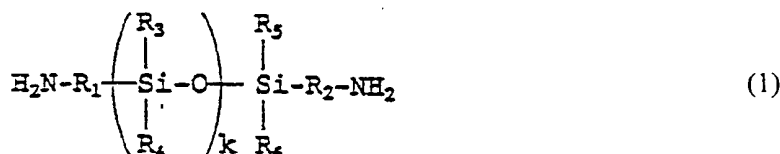
R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind und k eine ganze Zahl von 1-20 ist,

(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Bis-(aminophenoxy)-benzol und/oder ein Dimethylphenylendiamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

18. Ein Verfahren zur Herstellung eines Klebstofffilms, umfassend das Aufbringen, auf einer Seite oder beiden Seiten eines Substrats, einer Lösung in einem organischen Lösungsmittel eines Polyimidharzes mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, wobei das Polyimidharz erhalten wird durch Umsetzung von
- (B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



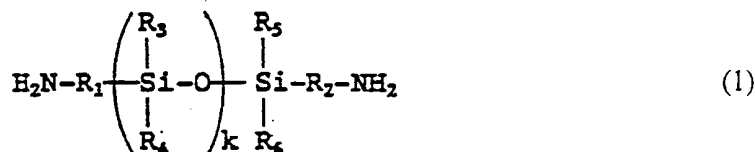
wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind, und k eine ganze Zahl von 1-20 ist,

(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und ein Dimethylphenylendiamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

19. Ein Verfahren zur Herstellung eines Klebstofffilms, umfassend das Aufbringen, auf einer Seite oder beiden Seiten eines Substrats, einer Lösung in einem organischen Lösungsmittel eines Polyimidharzes mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, wobei das Polyimidharz erhalten wird durch Umsetzung von
- (B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten



wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind, und k eine ganze Zahl von 1-20 ist,

(D) ein Bis-(aminophenoxy)-benzol und 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Dimethylphenylendiamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

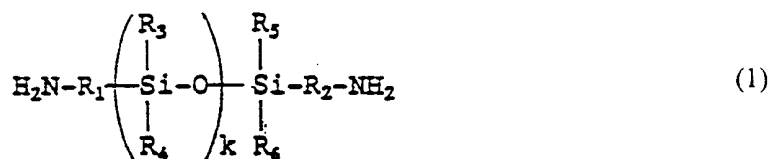
20. Ein Verfahren zur Herstellung eines Klebstofffilms, umfassend das Aufbringen, auf einer Seite oder beiden Seiten eines Substrats, einer Lösung in einem organischen Lösungsmittel eines Polyimidharzes mit einer Glasübergangstemperatur von 350°C oder darunter und löslich in organischen Lösungsmitteln, wobei das Polyimidharz erhalten wird durch Umsetzung einer Kombination der nachstehenden Säure-Komponenten (A) und (B)

(A) 4,4'-Oxydiphthalsäuredianhydrid

(B) 3,3',4,4'-Biphenyltetracarbonsäuredianhydrid und/oder 3,3',4,4'-Benzophenontetracarbonsäuredianhydrid

mit einer Kombination der nachstehenden Amin-Komponenten (C) und (D)

(C) 60 bis 5 Mol-% einer Siloxanverbindung der nachstehenden allgemeinen Formel (1), bezogen auf die Gesamtmenge der Amin-Komponenten

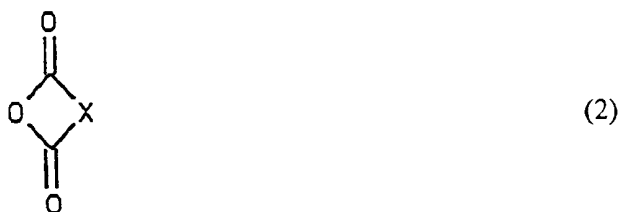


wobei die Reste R_1 und R_2 jeweils ein zweiwertiger aliphatischer (C_{1-4}) oder aromatischer Rest sind, die Reste R_3 , R_4 , R_5 und R_6 jeweils ein einwertiger aliphatischer oder aromatischer Rest sind, und k eine ganze Zahl von 1-20 ist,

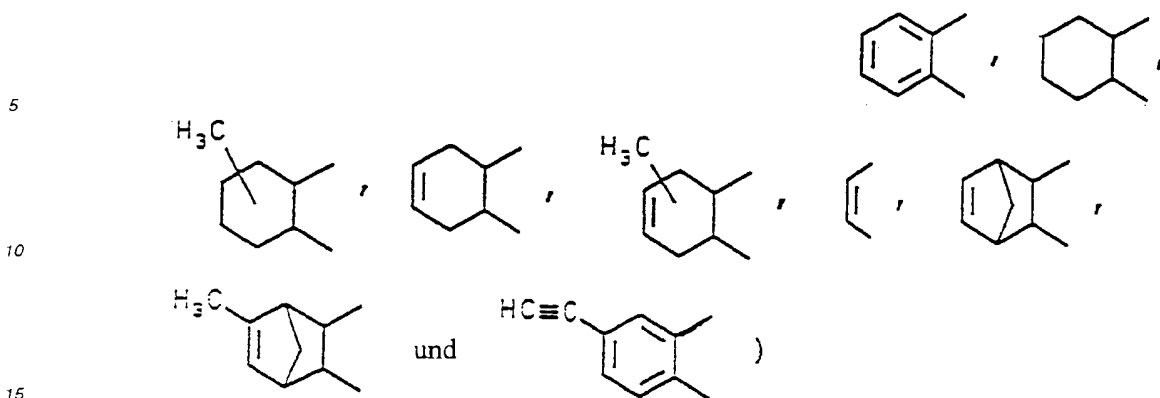
(D) 2,2-Bis-(4-(4-aminophenoxy)-phenyl)-propan und/oder ein Bis-(aminophenoxy)-benzol und/oder ein Dimethylphenylendiamin, und

Überführen der erhaltenen Polyamidsäure in das Polyimidharz.

21. Verfahren zur Herstellung eines Klebstofffilms gemäß einem der Ansprüche 17 bis 20, wobei das Polyimidharz an seinen Molekülen abgeschlossen ist mit einem Säureanhydrid der nachstehenden allgemeinen Formel (2)



wobei der Rest X mindestens ein Rest ist, ausgewählt aus der Gruppe von



oder einem aromatischen Amin der nachstehenden allgemeinen Formel (3)



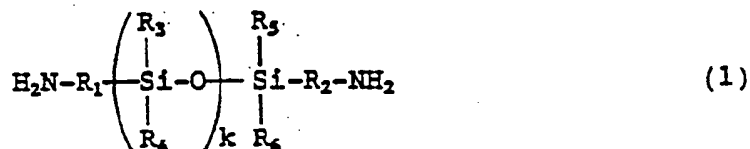
wobei der Rest Y mindestens ein Rest ist, ausgewählt aus Wasserstoffatomen und Methyl-, Ethyl-, Propyl-, Butyl-, Phenyl-, Methoxy-, Ethoxy-, Propoxy-, Butoxy- und Phenoxyresten.

22. Verfahren zur Herstellung eines Klebstofffilms gemäß einem der Ansprüche 17 bis 21, wobei das Substrat ein Polyimidfilm ist mit einer Glasübergangstemperatur von 350°C oder höher.
23. Verfahren zur Herstellung eines Klebstofffilms gemäß einem der Ansprüche 17 bis 21, umfassend das Abziehen des Substrats nach dem Aufbringen und Trocknen.
24. Verfahren nach Anspruch 23, wobei das Substrat ein biaxial gestreckter Polyesterfilm ist.
25. Verfahren zur Herstellung eines Klebstofffilms gemäß einem der Ansprüche 17 bis 24, umfassend das Aufbringen der Polyimidharz-Lösung auf ein Substrat unter Verwendung eines organischen Lösungsmittels mit einem Siedepunkt von 180°C oder darunter, Trocknen der Gieß-Polyimidharz-Lösung und Abziehen des getrockneten Polyimidharzes von dem Substrat.

Revendications

1. Résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, que l'on peut obtenir en faisant réagir
- (A) le dianhydride d'acide 4,4'-oxydiphthalique
- avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

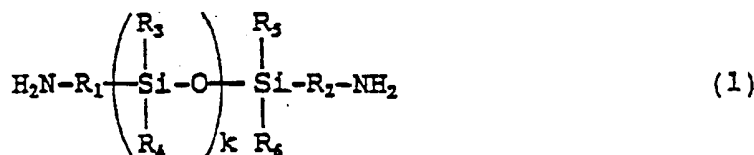
(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou un bis(aminophénoxy)benzène et/ou une diméthylphénylènediamine, à condition que le 2,2-bis(4-(4-aminophénoxy)phényl)propane ne soit pas le seul constituant (D), et

en convertissant le poly(acide amidique) obtenu en résine de polyimide.

2. Résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, que l'on peut obtenir en faisant réagir

(B) le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique
avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

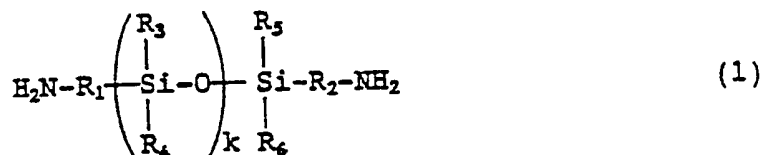
(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et une diméthylphénylènediamine, et

en convertissant le poly(acide amidique) obtenu en résine de polyimide.

3. Résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, que l'on peut obtenir en faisant réagir

(B) le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique
avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

(D) un bis(aminophénoxy)benzène et le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou une diméthylphénylènediamine, et

en convertissant le poly(acide amidique) obtenu en résine de polyimide.

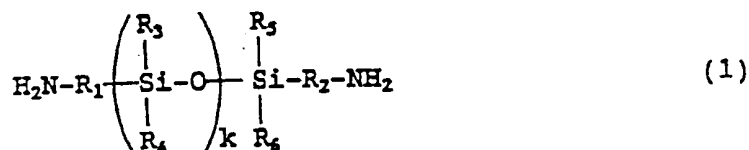
4. Résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble

dans des solvants organiques, que l'on peut obtenir en faisant réagir une combinaison des constituants acides (A) et (B) suivants

- (A) le dianhydride d'acide 4,4'-oxydiphthalique
(B) le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique

avec une combinaison des constituants amine (C) et (D) suivants

- (C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

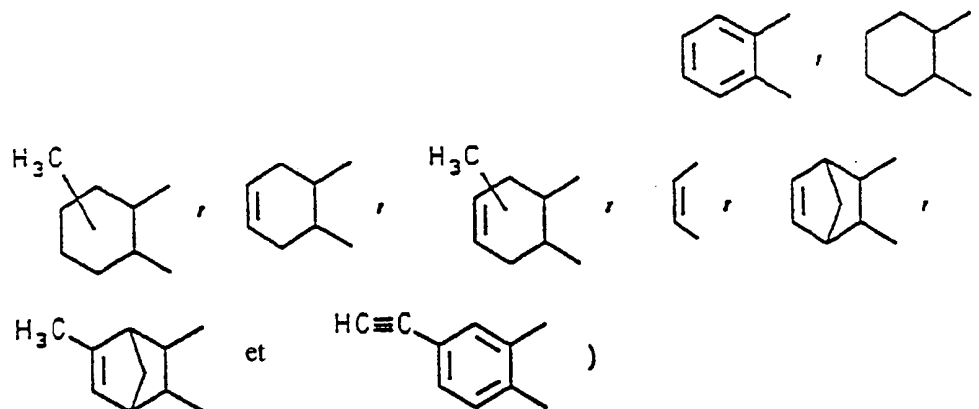
(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou un bis(aminophénoxy)benzène et/ou une diméthylphénylènediamine, et

en convertissant le poly(acide amidique) obtenu en résine de polyimide.

5. Résine de polyimide selon l'une quelconque des revendications 1 à 4, dont les extrémités moléculaires sont coiffées par un anhydride d'acide représenté par la formule générale (2) suivante



(X est au moins un groupe choisi parmi:



ou par une amine aromatique représentée par la formule générale (3) suivante



dans laquelle Y est au moins un groupe choisi parmi l'atome d'hydrogène, et les groupes méthyle, éthyle, propyle, butyle, phényle, méthoxy, éthoxy, propoxy, butoxy et phénoxy.

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6. Résine de polyimide selon la revendication 1 ou 4, dans laquelle la résine de polyamide est constituée à l'aide du constituant acide (A), à savoir le dianhydride d'acide 4,4'-oxydiphthalique, à raison de 60% en moles ou plus, par rapport à la quantité totale des constituants acides.
- 15
7. Résine de polyimide selon l'une quelconque des revendications 2 à 4, dans laquelle la résine de polyimide est constituée, en tant que constituant acide (B), de p moles de dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et de q moles de dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique, dans des proportions satisfaisant à $0,5 \leq p/(p+q) \leq 0,9$
- 20
8. Résine de polyimide selon l'une quelconque des revendications 1, 3 et 4, dans laquelle la résine de polyimide est constituée, en tant que constituants amine (D), du 1,3-bis(3-aminophénoxy)benzène, à raison de 10-90% en moles, par rapport à la quantité totale des constituants amine.
- 25
9. Résine de polyimide selon la revendication 4, dans laquelle la résine de polyimide est constituée, en tant que constituants acides, de a moles de dianhydride d'acide 4,4'-oxydiphthalique et de b moles d'un autre dianhydride d'acide tétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylène-diamine et de e moles d'une autre diamine, dans des proportions satisfaisant à $a/(a+b) \geq 0,6$, $0,6 > b/(a+b) \geq 0$, $0,1 \leq c/(c+d+e) \leq 0,6$, $0,6 \leq (c+d)/(c+d+e)$, $0 \leq e/(c+d+e) < 0,6$ et $0,950 < (a+b)/(c+d+e) < 1,02$.
- 30
10. Résine de polyimide selon la revendication 4, dans laquelle la résine de polyimide est constituée, en tant que constituants acides, de a moles de dianhydride d'acide 4,4'-oxydiphthalique et de b moles d'un autre dianhydride d'acide tétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylènediamine et de e moles d'une autre diamine, et dont les extrémités moléculaires sont coiffées par f moles d'un anhydride d'acide représenté par la formule générale (2) ou par g moles d'une amine aromatique représentée par la formule générale (3), et dans laquelle les rapports molaires de a, b, c, d, e, f et g satisfont à $0,6 \leq a/(a+b+0,5f)$, $0 \leq b/(a+b+0,5f) < 0,6$, $0,1 \leq c/(c+d+e+0,5g) \leq 0,6$, $0 \leq e/(c+d+e) < 0,6$, $0,01 \leq f/(a+b+0,5f) \leq 0,05$ et $0,01 \leq g/(c+d+e+0,5g) \leq 0,05$ et soit f soit g est nul.
- 35
- 40
11. Résine de polyimide selon la revendication 2 ou 3, dans laquelle la résine de polyimide est constituée, en tant que constituants acides, de p moles de dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et de q moles de dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de c' moles de 2,2-bis(4-(4-aminophénoxy)phényl)propane et de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylènediamine, de sorte que les rapports molaires de p, q, c, c' et d satisfont à $0,5 \leq p/(p+q) \leq 0,9$, $0,1 \leq q/(p+q) \leq 0,5$ et $0,05 \leq c/(c+c'+d) \leq 0,5$.
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12. Résine de polyimide selon la revendication 2 ou 3, dans laquelle la résine de polyimide est constituée, en tant que constituants acides, de p moles de dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et de q moles de dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de c' moles de 2,2-bis(4-(4-aminophénoxy)phényl)propane et de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylènediamine, et dont les extrémités moléculaires sont coiffées par f moles d'un anhydride d'acide représenté par la formule générale (2) ou par g moles d'une amine aromatique représentée par la formule générale (3), et dans laquelle les rapports molaires de p, q, c, c', d, f et g satisfont à $0,5 \leq p/(p+q+0,5f) \leq 0,9$, $0,1 \leq q/(p+q+0,5f) \leq 0,5$, $0,05 \leq c/(c+c'+d+0,5g) \leq 0,5$, $0,01 \leq f/(p+q+0,5f) \leq 0,05$ et $0,01 \leq g/(c+c'+d+0,5g) \leq 0,05$ et soit f soit g est nul.
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13. Résine de polyimide selon la revendication 4, dans laquelle la résine de polyimide est constituée, en tant que

constituants acides, de a moles de dianhydride d'acide 4,4'-oxydiphthalique et de b moles d'un ou de deux dianhydrides d'acide tétracarboxylique choisis dans le groupe constitué par le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de c' moles de 2,2-bis(4-(4-aminophénoxy)phényl)propane et de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylènediamine, de sorte que les rapports molaires de a, b, c, c' et d satisfont à $a/(a+b) \geq 0,6$, $b/(a+b) \leq 0,4$ et $0,05 \leq c/(c+c'+d) \leq 0,5$.

14. Résine de polyimide selon la revendication 4, dans laquelle la résine de polyimide est constituée, en tant que constituants acides, de a moles de dianhydride d'acide 4,4'-oxydiphthalique et de b moles d'un ou de deux dianhydrides d'acide tétracarboxylique choisis dans le groupe constitué par le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique et, en tant que constituants amine, de c moles d'un composé siloxane représenté par la formule générale (1), de c' moles de 2,2-bis(4-(4-aminophénoxy)phényl)propane et de d moles de 1,3-bis(3-aminophénoxy)benzène et/ou de diméthylphénylènediamine, et dont les extrémités moléculaires sont coiffées par f moles d'un anhydride d'acide représenté par la formule générale (2) ou par g moles d'une amine aromatique représentée par la formule générale (3), et dans laquelle les rapports molaires de a, b, c, c', d, f et g satisfont à $a/(a+b+0,5f) \geq 0,6$, $b/(a+b+0,5f) \leq 0,4$, $0,05 \leq c/(c+c'+d+0,5g) \leq 0,5$, $0,01 \leq f/(a+b+0,5f) \leq 0,05$ et $0,01 \leq g/(c+c'+d+0,5g)$ et soit f soit g est nul.

15. Film adhésif comprenant un film de base résistant à la chaleur et une résine de polyimide selon l'une quelconque des revendications 1 à 14, appliquée sur une face ou sur les deux faces du film de base.

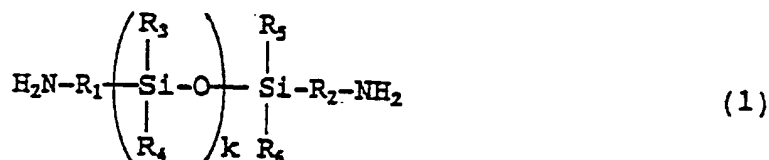
16. Film adhésif selon la revendication 15, dans lequel le film de base résistant à la chaleur est un film de polyimide ayant une température de transition vitreuse de 350°C ou plus élevée.

17. Procédé de production d'un film adhésif qui comprend le fait de couler, sur une face ou sur les deux faces d'un substrat, une solution dans un solvant organique d'une résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, ladite résine de polyimide pouvant être obtenue par réaction

(A) du dianhydride d'acide 4,4'-oxydiphthalique

avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine;



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou un bis(aminophénoxy)benzène et/ou une diméthylphénylènediamine, et

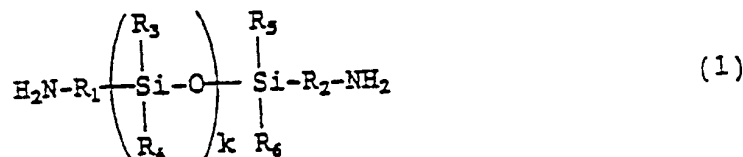
de convertir le poly(acide amidique) obtenu en résine de polyimide.

18. Procédé de production d'un film adhésif qui comprend le fait de couler, sur une face ou sur les deux faces d'un substrat, une solution dans un solvant organique d'une résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, ladite résine de polyimide pouvant être obtenue par réaction

(B) du dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou du dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique

avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et une diméthylphénylènediamine, et

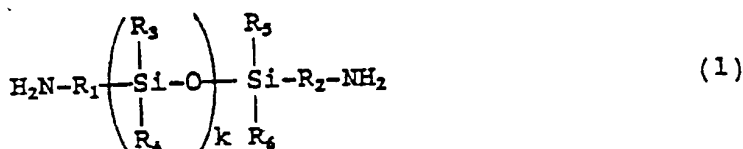
de convertir le poly(acide amidique) obtenu en résine de polyimide.

19. Procédé de production d'un film adhésif qui comprend le fait de couler, sur une face ou sur les deux faces d'un substrat, une solution dans un solvant organique d'une résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, ladite résine de polyimide pouvant être obtenue par réaction

(B) du dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou du dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique

avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine:



dans laquelle R_1 et R_2 représentent chacun un groupe aliphatique en C_1 - C_4 ou aromatique bivalent; R_3 , R_4 , R_5 et R_6 représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

(D) un bis(aminophénoxy)benzène et le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou une diméthylphénylènediamine, et

de convertir le poly(acide amidique) obtenu en résine de polyimide.

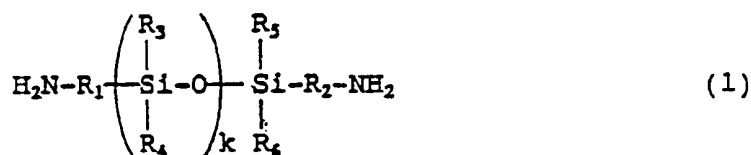
20. Procédé de production d'un film adhésif qui comprend le fait de couler, sur une face ou sur les deux faces d'un substrat, une solution dans un solvant organique d'une résine de polyimide qui possède une température de transition vitreuse de 350°C ou plus basse et qui est soluble dans des solvants organiques, ladite résine de polyimide pouvant être obtenue par réaction d'une combinaison des constituants acides (A) et (B) suivants

(A) le dianhydride d'acide 4,4'-oxydiphthalique

(B) le dianhydride d'acide 3,3',4,4'-biphényltétracarboxylique et/ou le dianhydride d'acide 3,3',4,4'-benzophénonetétracarboxylique

avec une combinaison des constituants amine (C) et (D) suivants

(C) 60 à 5% en moles d'un composé siloxane représenté par la formule générale (1) suivante, par rapport à la quantité totale des constituants amine



dans laquelle R₁ et R₂ représentent chacun un groupe aliphatique en C₁-C₄ ou aromatique bivalent, R₃, R₄, R₅ et R₆ représentent chacun un groupe aliphatique ou aromatique monovalent; et k est un nombre entier de 1 à 20;

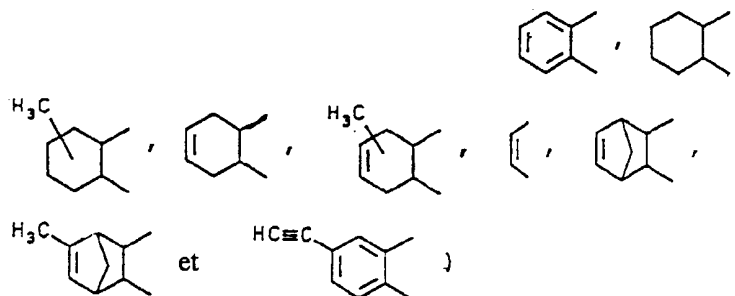
(D) le 2,2-bis(4-(4-aminophénoxy)phényl)propane et/ou un bis(aminophénoxy)benzène et/ou une diméthylphénylènediamine, et

de convertir le poly(acide amidique) obtenu en résine de polyimide.

21. Procédé de production d'un film adhésif selon l'une quelconque des revendications 17 à 20, dans lequel les extrémités moléculaires de la résine de polyimide sont coiffées par un anhydride d'acide représenté par la formule générale (2) suivante



(X est au moins un groupe choisi parmi:



ou par une amine aromatique représentée par la formule générale (3) suivante



dans laquelle Y est au moins un groupe choisi parmi l'atome d'hydrogène, et les groupes méthyle, éthyle, propyle, butyle, phényle, méthoxy, éthoxy, propoxy, butoxy et phénoxy.

22. Procédé de production d'un film adhésif selon l'une quelconque des revendications 17 à 21, dans lequel le substrat est un film de polyimide ayant une température de transition vitreuse de 350°C ou plus élevée.

23. Procédé de production d'un film adhésif selon l'une quelconque des revendications 17 à 21, qui comprend le fait

de décoller le substrat après le coulage et le séchage.

24. Procédé selon la revendication 23, dans lequel le substrat est un film de polyester étiré biaxialement.

5 25. Procédé de production d'un film adhésif selon l'une quelconque des revendications 17 à 24, qui comprend le fait de couler ladite solution de résine de polyimide sur un substrat à l'aide d'un solvant organique ayant un point d'ébullition de 180°C ou plus bas, de sécher la solution de résine de polyimide coulée et de décoller du substrat la résine de polyimide séchée.

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